ASSIGNMENT OF THE BANDS IN THE UV SPECTRA OF MONO- AND DINITRO-1,2,3,4-TETRAHYDROQUINOLINES AND DETERMINATION OF THE PREDOMINANT CONFORMATIONS OF THEIR N-SUBSTITUTED DERIVATIVES

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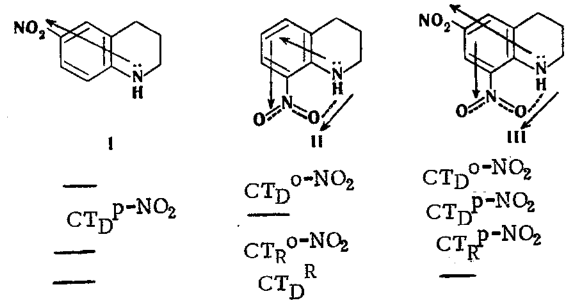
On the basis of the principle of resolving the structure of a molecule into its initial polar chromophoric systems and the method of comparative spectroscopy, an assignment of bands in the electronic spectra of 6-nitro-, 8-nitro-, and 6,8-dinitro-1,2,3,4-tetrahydroquinolines and their N-alkyl and N-acyl derivatives has been made. The electronic spectra have been used to establish the predominant conformations of sterically hindered compounds.

The method of quasi-autonomous systems of assigning the absorption bands in the electronic absorption spectra (EASs) of polysubstituted benzenes of the donor-acceptor type (DA type) proposed previously by one of us [1] has been used for some nitrogen-containing heterocycles. The method permits the assignment of the bands to be made without having recourse to quantum-chemical calculations. In the present work we set ourselves the task of assigning the bands in the EASs of mono- and dinitro derivatives of 1,2,3,4-tetrahydroquinoline (THQ), i.e., of establishing between which fragments of the molecule there is a redistribution of electron density for each electronic transition. The objects of investigation were 6-nitro-THQ (I), 8-nitro-THQ (II), 6,8-dinitro-THQ (III), and their N-alkyl and N-acyl derivatives. Tables 1-3 give the values of λ_{max} and ε_{max} of the charge-transfer (CT) bands of the nitro derivatives of THQ and their N-substituted derivatives obtained experimentally and their respective assignments according to [1]. For comparison, the same Tables give the assignments of the bands in the EASs of the 2-nitro-, 4-nitro-, and 2,4-dinitroanilines, and their N-substituted derivatives, with analogous structures which have been studied previously [1, 2].* It is known that steric hindrance leading to the rotation of a substituent around the substituent–ring bond causes a reduction in the intensity of the CT bands with the participation of these groups [3]. On the basis of a comparison of the EASs of almost planar systems with the EASs of sterically overstrained molecules it is possible to deduce the predominant conformations of sterically hindered compounds. In contrast to the sterically N-substituted nitroanilines considered previously, in the N-substituted heterocycles (I-III) the amino group is fixed. Consequently, we set ourselves simultaneously the task of investigating the spectral and conformational characteristics of these compounds.



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*The molecules of the 2-methyl-N-alkyl- and 2-methyl-N,N-dialkylnitroanilines cannot be considered as standard compounds for the N-substituted nitrogeneous heterocycles (I-III), since there is great steric hindrance between the N-alkyl and 2-methyl groups in them.

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TABLE 1. Electronic Absorption Spectra in Ethanol ($c = 10^{-4}$–10^{-5} M)

Compound	Symbol in the text	$CT_D^{p\text{-}NO_2}$ band	
		λ, nm	ε, liter • mole^{-1} • cm^{-1}
$4\text{-}O_2NC_6H_4NHEt$	IV	390	19000
$4\text{-}O_2NC_6H_4NEt_2$	V	395	21800
$4\text{-}O_2NC_6H_4NHCOMe$	VII	315	13500
$4\text{-}O_2NC_6H_4NMeAc$	XII	286	7800
$C\text{-}NO_2\text{-}THQ$	I	404	17200
$6\text{-}NO_2\text{-}N\text{-}Pr\text{-}THQ$	VI	385	16600
$6\text{-}NO_2\text{-}N\text{-}Formyl\text{-}THQ$	VIII	335	11900
$6\text{-}NO_2\text{-}N\text{-}Ac\text{-}THQ$	IX	340	12100
$6\text{-}NO_2\text{-}N\text{-}Benzoyl\text{-}THQ$	X	325	10400
$6\text{-}NO_2\text{-}N\text{-}(2'\text{-}Chlorobenzoyl)\text{-}THQ$	XI	317	9000

TABLE 2. Electronic Absorption Spectra in Ethanol ($c = 10^{-4}$–10^{-5} M)

Compound	Symbol in the text	Charge-transfer bands					
		$CT_D^{o\text{-}NO_2}$		$CT_R^{o\text{-}NO_2}$		CT_D^R	
		λ, nm	ε, liter • mole^{-1} • cm^{-1}	λ, nm	ε, liter • mole^{-1} • cm^{-1}	λ, nm	ε, liter • mole^{-1} • cm^{-1}
$2\text{-}O_2NC_6H_4NHEt$	XIII	425	6200	280	4610	232	21000
$2\text{-}O_2NC_6H_4NMe_2$	XIV	416	2950	Masked		245	21500
$2\text{-}O_2NC_6H_4NHAc$	XIX	328	1900	269	2270	228	14500
Hexane		352	6150	274	6450	237	21400
$2\text{-}O_2NC_6H_4NMeAc$	XXII	~300	1000	Masked		~215	10000
$8\text{-}NO_2\text{-}THQ$	II	447	6700	294	5900	235	17000
$8\text{-}NO_2\text{-}N\text{-}Me\text{-}THQ$	XV	433	3000	295	4000	255	15800
$8\text{-}NO_2\text{-}N\text{-}Et\text{-}THQ$	XVI	430	2100	~295	2500	255	14400
$8\text{-}NO_2\text{-}N\text{-}Pr\text{-}THQ$	XVII	435	2700	Masked		255	11400
$8\text{-}NO_2\text{-}N\text{-}Bu\text{-}THQ$	XVIII	440	2300	Masked		255	11800
$8\text{-}NO_2\text{-}N\text{-}COCH_2Cl\text{-}THQ$	XX	325	2200	~270	3400	245	12100
$8\text{-}NO_2\text{-}N\text{-}COC_6H_5\text{-}THQ$	XXI	335	3000	Masked		242	18000

According to the method of quasi-autonomous systems [1] which is based on the principle of resolving the structure of a molecule into its initial polar chromophoric systems [4], in the EAS of compound (III), which is assigned to the 2,4-AA-1-D type, the CT bands of the initial disubstituted (I) and (II), of types 4-A-1-D and 2-A-1-D, respectively, should appear. Consequently, before considering the EASs of a compound (III) it is necessary to analyze the EASs of substances (I), (II), and their N-substituted derivatives.

In the EAS of substance (I) there is a strong band due to CT from the amino group to the p-NO_2 group ($CT_D^{p\text{-}NO_2}$) shifted bathochromically in comparison with the band of N-ethyl-4-nitroaniline (IV) and with a somewhat lower intensity, and also a shortwave band of the local excitation of the benzene ring of the $A_{1g} \rightarrow B_{1i}$ type (I and IV, Table 1). The lowering of the intensity of the CT bands in compound (I) shows that the axis of the P_z orbitals of the benzene ring and the amino group are not parallel in accordance with the stereochemical behavior of the THQ ring, which consists of a mixture of half-chair conformations passing into one another ($\theta = 18°$ according to Braude's formula [3]). The bathochromic shift of the CT band is due to the increase in the electron-donating properties of the ring because of the presence of an o-alkyl substituent in it.

The N-alkylation of a 4-nitromonoalkylaniline, causing no steric hindrance, leads to an increase in the donor capacity of the $NAlk_2$ group, which in the EAS of N,N-diethyl-4-nitroaniline (V) is shown in a bathochromic shift with a rise in the intensity of the $CT_D^{p\text{-}A}$ band. Consequently, the small hypsochromic shift with a decrease in intensity in 6-NO_2-N-propyl-THQ (VI) is connected with a further disturbance in the parallelism of the P_z orbitals of the nitrogen and the benzene ring ($\theta = 21°$) because of steric hindrance between the N-Pr and 8-H atoms (I, IV-VI, Table 1 and Fig. 1).

The replacement of the N-Alk group by an Ac group, i.e., the passage from compound (IV) to 4-NO_2-acetanilide (VII) leads to a pronounced hypsochromic shift with a reduction in in-

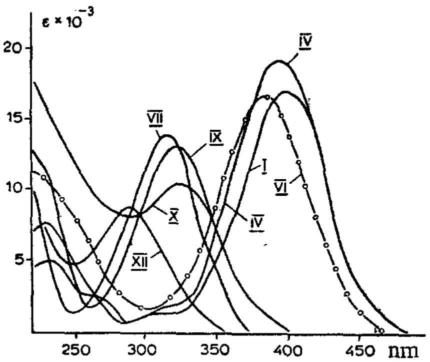

Fig. 1

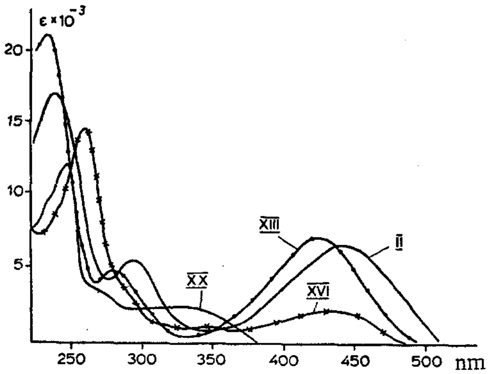

Fig. 2

Fig. 1. Electronic absorption spectra. The numbers of the curves correspond to the numbers of the compounds in Table 1.

Fig. 2. Electronic absorption spectra. The numbers on the curves correspond to the numbers of the compounds in Table 2.

tensity of the CT_D^{p-A} band. This cannot be caused solely by steric hindrance which is very small in compound (VII) since the angle between the planes of the benzene ring and the NHAc group cannot be greater than 17°36', as in N-acetanilide [5]. The reason is apparently a dispersion of the mesomeric effect of the unshared pair of the nitrogen atom through the carbonyl group. The hypsochromic shift with a reduction in the intensity of the CT_D^{p-A} band in the EASs of the 6-NO_2-N-Ac-THQs (VIII-XI) must also be explained by the dispersion of the mesomeric effect, but the CT band in the latter is located somewhat more bathochromically than for the benzene analog. This is connected with a decrease in the degree of dispersion of the mesomeric effect in compounds (VIII-XI), where the nitrogen atom is practically fixed and steric hindrance between N-Ac and 8-H is eliminated not by the rotation of an amino group but by the rotation of a N-Ac group (I, IV, VII-XI, Table 1 and Fig. 1).*

In the molecule of 8-nitro-THQ (II; 2-A-1-D type), as in the N-Alk-2-nitroaniline (XIII) there is an intramolecular hydrogen bond (intra-HB), a consequence of which is the location of the nitro group in the plane of the benzene ring. The intra-HB is confirmed by the lowering of ν_{NH} (CCl_4) of the ortho-substituted compounds in comparison with the para isomers: ν_{NH} (6-NO_2-THQ) 3460 cm^{-1}, ν_{NH} (8-NO_2-THQ) 3380 cm^{-1}. The EAS of compound (II) is analogous to that of a N-Alk-2NO_2-aniline and contains the same three absorption bands, which must be assigned to transitions from the NAlk group to the O-NO_2 group ($CT_D^{o-NO_2}$), from the ring to the 8-NO_2 group ($CT_R^{8-NO_2}$), and from NAlk to the ring (CT_D^R) (II and XIII, Table 2 and Fig. 2). The bathochromic shift of the CT bands in substance (II) as compared with (XIII) is a consequence of the increase in the electron-donating capacity of the ring because of the presence of o-Alk groups, and the lowering of the intensity of the CT_D^R band is a consequence of the parallelism of the P_z orbitals of the nitrogen atom and of the ring. The N-alkylation of compounds (II) and (XIII) leads to the elimination of the intra-HB fixing the substituent in the plane of the ring and to pronounced steric hindrance between the N-alk and o-NO_2 groups, a consequence of which is the reduction in the intensity of the CT_D^{o-A} and CT_R^A bands in the EAS. Analysis of the EASs shows that in both cases the steric hindrance is eliminated mainly by rotation around the C—N bond of the nitro group by an average of 50° (II, XIII-XVIII, Table 2 and Fig. 2).

The N-acylation of 2-nitroaniline leads to a hypsochromic shift of all the CT bands with a marked reduction in intensity. However, these changes are connected not only with a decrease in the donor properties of the amino group but also with a disturbance in ethanol with the planarity of the molecule because of the cleavage of the intra-HB that existed in hexane and the formation of a solvated complex [7, 8] (XIII and XIX, Table 2). The N-acylation of 8-NO_2-THQ leads to similar changes in the spectrum (II, XX, and XXI, Table 2 and Fig. 2).

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*A comparison of the EAS of 6-NO_2-N-Ac-THQ with the EAS of N-acetyl-N-methyl-4-nitroaniline (XII) is unjustified, since in the latter, as in N-methylacetanilide, there is considerable steric hindrance; the MeCONMe group is almost orthogonal to the benzene ring [6-8] and the spectrum of this compound is almost similar to the EAS of nitrobenzene (IV, VII, XII, Table 1 and Fig. 1).

TABLE 3. Electronic Absorption Spectra in Ethanol (c = 10^{-4}-10^{-5} M)

Compound	Symbol in the text	Charge-transfer bands					
		$CT_D^{o-NO_2}$		$CT_R^{p-NO_2}$		$CT_R^{o-NO_2}$	
		λ, nm	ε, liter · mole⁻¹ · cm⁻¹	λ, nm	ε, liter · mole⁻¹ · cm⁻¹	λ, nm	ε, liter · mole⁻¹ · cm⁻¹
2,4-$(NO_2)_2C_6H_3NHEt$	XXIII	~410	6700	347	16600	260	8900
Hexane		390	5400	326	17200	250	9300
2,4-$(NO_2)_2C_6H_3NEt_2$	XXV	Masked		375	16600	Masked	
2,4-$(NO_2)_2C_6H_3NHAc$	XXVIII	—	—	302	10600	—	—
6,8-$(NO_2)_2$-THQ	III	420	6600	360	15800	270	10000
6,8-$(NO_2)_2$-N-Et-THQ	XXIV	—	—	378	18600	—	—
6,8-$(NO_2)_2$-N-CHO-THQ	XXVI	410	10600	365	17700	270	9800
6,8-$(NO_2)_2$-N-Ac-THQ	XXVII	410	10200	365	17400	270	9800

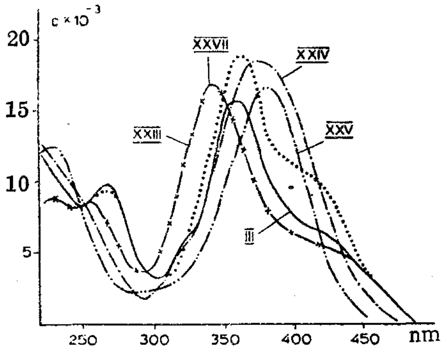
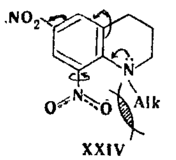


Fig. 3. Electronic absorption spectra. The numbers on the curves correspond to the numbers of the compounds in Table 3.

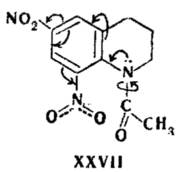
The presence of a long-wave band of low intensity in the spectra of compounds (XX and XXI) shows a residual transfer of charge between the D and o-A groups in spite of the pronounced rotation of the ortho substituents. Steric hindrance in the N-Ac-N-Me-2-nitroaniline molecule (XXII) is expressed even more strongly than in (XIX and XXII), Table 2.

The molecule of 6,8-dinitro-THQ, like those of N-alkyl-2,4-dinitroanilines, is planar since an intra-HB exists between the NH and 8-NO_2 groups (ν_{NH} 3370 cm^{-1}, CCl_4). The molecule of 6,8-dinitro-THQ (III) is similar to a benzene derivative of the 2,4-AA-1-D type. In accordance with the method of quasi-autonomous systems [1], the EAS of substance (III) should be composed of the CT bands of the initial systems of (I) and (II). On summing the bands, no account was taken of the CT_D^R band of system (II). In the EAS of compound (III), the three CT bands of the initial system, somewhat shifted in comparison with their positions in the disubstituted compounds, should be present. All three bands are actually present in the EAS of substance (III): the band of CT from the donor to the o-NO_2 group (CT_D^{o-A}), the band of CT from the donor to the p-NO_2 group (CT_D^{p-A}), and the band of CT from the ring to the o-NO_2 group (CT_R^A). The EAS of compound (III) is almost identical with that of N-ethyl-2,4-dinitroaniline [1, 2] (XXIII) (Table 3 and Fig. 3).

The N-alkylation of compound (III) eliminates the intra-HB and interferes with the planarity of the molecule. It may be assumed that because of the fixation of the N-Alk group steric strain will be eliminated by the rotation of the NO_2 group around the C—N bond. Marked rotation of the NO_2 group may cause a decrease in the EAS of the CT bands in which it participates, namely $CT_D^{8-NO_2}$ and $CT_R^{8-NO_2}$.



XXIV



XXVII

The EAS of N-ethyl-6,8-dinitro-THQ (XXIV) completely confirms our hypotheses. In the EAS of this compound the $CT_D^{8-NO_2}$ and $CT_R^{8-NO_2}$ bands are practically absent and only the $CT_D^{6-NO_2}$ band, bathochromically shifted in comparison with the band of compound (III) and with an increased intensity (system 4-A-1-D), is present. The EAS is similar to that of compound (VI) (III and XXIV, Table 3, Fig. 3; VI, Table 1). One of us has established previously [2] that the introduction of a second Alk group into a N-Alk-2,4-dinitroaniline leads to surprising changes in the spectrum: in spite of the steric hindrance a bathochromic shift of the p-band ($CT_D^{p-NO_2}$) is observed, and the $CT_D^{o-NO_2}$ and $CT_R^{o-NO_2}$ bands undergo such a reduction in intensity that they do not appear in the EAS and the spectrum is similar to that of 4-nitroaniline. This was due to the fact that the steric hindrance in N,N-dialkyl-2,4-dinitroaniline (XXV) is eliminated mainly by rotation of the 2-NO_2 group. The similarity of the EASs of compounds (XXIV) and (XXV) shows the identity of their conformations, while, if the favorable conformation of the molecule of (XXIV) is readily explainable, the reason leading to the analogous conformation of compound (XXV) requires elucidation. The conjugation of the $NAlk_2$ group with the 4-NO_2 group in the molecule of (XXV) increases the rigidity of the C—$NAlk_2$ bond (buttressing effect [1, 9]), and therefore it is considerably easier for the 2-NO_2 group, not conjugated in the para position with the complementary substituent to depart from the plane of the molecule with the retention of the coplanarity of the $NAlk_2$ group. In the EAS of the sterically hindered compounds (XXIV and XXV) a bathochromic shift of the CT_D^{p-A} band is observed in comparison with the EAS of compound (III). Both in the molecule of (XXV) and in that of (XXIV) the "steric enhancement of resonance effect" exists [10]. Because of the rotation of the 2-NO_2 or 8-NO_2 group its acceptor properties diminish, which leads to an increase in the electron density of the nitrogen atom and of the benzene ring and, hence, to a bathochromic shift of the CT_D^{p-A} band, in spite of steric hindrance.

The EASs of the N-Ac-6,8-dinitro-THQs (XXVI and XXVII) are practically identical with those of the unsubstituted 6,8-dinitro-THQ (III). This shows that steric hindrance in this molecule is eliminated by rotation of the N-Ac group, while the 8-NO_2 group remains practically in the plane of the benzene ring. The conformation of the (XXVII) molecule differs greatly from that of N-Ac-2,4-dinitroaniline (XXVIII), in which the NHAc group is located in the plane of the ring because of the existence of an intra-HB (in hexane), although in ethanol this bond is cleaved, forming an inter-HB, with the appearance of steric hindrance (XXIII and XXVIII, Table 3).

Thus, the method of quasi-autonomous systems proposed for benzene derivatives is also applicable to the interpretation of EASs and to the establishment of conformations and conformational features of derivatives of nitro- and dinitro-THQs.

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