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## MOLECULAR COMPLEXES OF AROMATIC N-OXIDES WITH TETRACYANOETHYLENE

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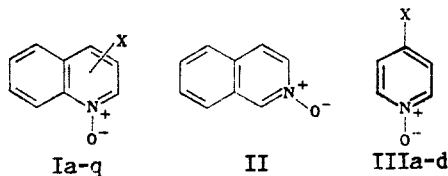
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*Donor—acceptor interaction of tetracyanoethylene with aromatic N-oxides leads to the formation of two kinds of molecular complexes of the  $\pi,\pi$ -type:  $\pi$ -complexes and charge-transfer complexes. A correlation is observed between the reactivity of the N-oxides and the electronic properties of the substituents in the N-oxides.*

Heterocyclic N-oxides can be regarded as nitrones, the dipolar function of which enters in part into the aromatic system. As a consequence, in reactions of N-oxides with dipolarophiles it is necessary to consider both their capability of 1,3-dipolar cycloaddition and the possibility of forming donor—acceptor complexes [1].

We studied the interaction of aromatic N-oxides with tetracyanoethylene (TCE), which seems, on one hand, to be an extremely active dipolarophile, and on the other, a strong  $\pi$ -acceptor [2, 3].

We have investigated the interaction with TCE of aromatic N-oxides of quinolines (Ia-g), isoquinoline (II), and pyridines (IIIa-d), containing both electron—acceptor and electron—donor substituents:



I a) X=4-NO<sub>2</sub>, b) X=4-Cl, c) X=H, d) X=4-CH<sub>3</sub>, e) X=4-SCH<sub>3</sub>, f) X=4-OCH<sub>3</sub>, g) X=2-CH<sub>3</sub>,  
 III a) X=OCH<sub>3</sub>, b) X=N-morpholy1, c) X=OH, d) X=ONa

### $\pi$ -COMPLEXES

It was established that the interaction of the N-oxides Ib-g, II, and IIIa, b, d with TCE initially leads to the formation of colored "weak" complexes that exist only in solution in equilibrium with the original components. In the UV spectra of these  $\pi$ -complexes (Fig. 1), new "charge transfer" bands appear, but the positions of the absorption bands of the original components remain unchanged. By the continuous variation method [4] we found the equilibrium constants for the formation of  $\pi$ -complexes ( $K_{\pi}^{\text{eq}}$ ), and we also showed that their composition corresponds to 1:1 stoichiometry (Table 1).

The equilibrium constants of  $\pi$ -complex formation for the N-oxides Ib-f show a linear correlation with the  $\sigma_n^+$  constants of the substituents:

$$\lg K_{\pi}^{\text{eq}} = \lg K_0^{\text{eq}} + \rho \sigma_n^+,$$

where  $K_1^{\text{eq}}$  and  $K_0^{\text{eq}}$  are the equilibrium constants of  $\pi$ -complexation of the substituted and unsubstituted quinoline N-oxides, respectively;  $\rho$  is the reaction constant;  $\sigma_n^+$  is the Hammett constant for the para-substituent. The slope of the straight-line plot (Fig. 2) gives  $\rho = -0.84$  (20°C, CHCl<sub>3</sub>). The negative value of  $\rho$  indicates that the N-oxides manifest electron—donor properties in this reaction; the relatively large value of  $\rho$  indicates a large demand of the

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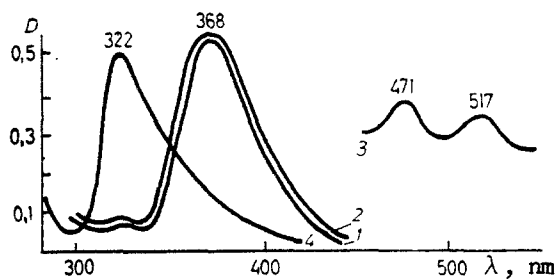


Fig. 1

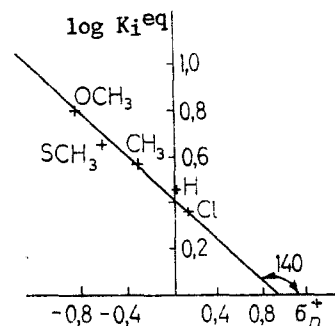


Fig. 2

Fig. 1. UV spectra: 1) quinoline N-oxide; 2)  $\pi$ -complex of quinoline N-oxide and TCE, 1:1; 3)  $\pi$ -complex of quinoline N-oxide and TCE, 1:10; 4) charge-transfer complex of quinoline N-oxide and TCE.

Fig. 2. Rate constant of  $\pi$ -complexation of 4-substituted quinoline N-oxides with TCE, as a function of  $\sigma_n^+$  Hammett constant.

TABLE 1.  $\pi$ -Complexes of N-Oxides with TCE

N-Oxide	$\lambda$ of "charge transfer" band, nm (chloroform)	$\epsilon$	$K^{eq}$	N-Oxide	$\lambda$ of "charge transfer" band, nm (chloroform)	$\epsilon$	$K^{eq}$
Ib	490	60,8	2,38	If	522	70,3	6,15
Ic	498	61,8	2,84	Ig	510	33,8	2,71
Id	504	65,0	3,35	II	448	120,3	5,31
Ie	555	150,8	4,60	III a	425	300,0	—

TABLE 2. Characteristics of  $\pi$ -Complexes of Quinoline N-Oxide and TCE, in Different Solvents

Solvent	$\lambda$ , nm	$\epsilon$	$K^{eq}$ , mole $^{-1}$
Diethyl ether	477	155,0	4,47
Chloroform	498	61,8	2,84
Acetonitrile	471, 517	Insignificant	Insignificant

TABLE 3. Charge-Transfer Complexes of N-Oxides with TCE

N-Oxide	N-Oxide:TCE ratio	Crystallization time, h	Melting point, °C	N found, %	$\nu_{C\equiv N}$ , cm $^{-1}$	CTC color	Yield, %
Ib	1:0,36	48	123	15,20	2230	Reddish brown	21...25
Ic	1:0,35	24	133...134	17,96	2220	Light gray	44...52
Id	1:0,34	24	142...144	16,26	2218	Light gray	55...57
Ie	1:0,66	24	182	18,56	2218	Yellow	55
If	1:0,66	1	180...181	19,64	2210	Yellow	61...66
Ig	1:0,33	24	147...148	16,11	2202	Colorless	46...65
II	1:0,39	2	161...162 (dec.)	18,46	2230	Yellow	38...50
IIIa	1:0,59	24	128	23,50	2207	Yellow	53...55
IIIb	1:0,78	0,25	149 (dec.)	25,63	2190	Yellow	84...90
IIIc	—	1	280 (dec.)	—	—	Yellow	26

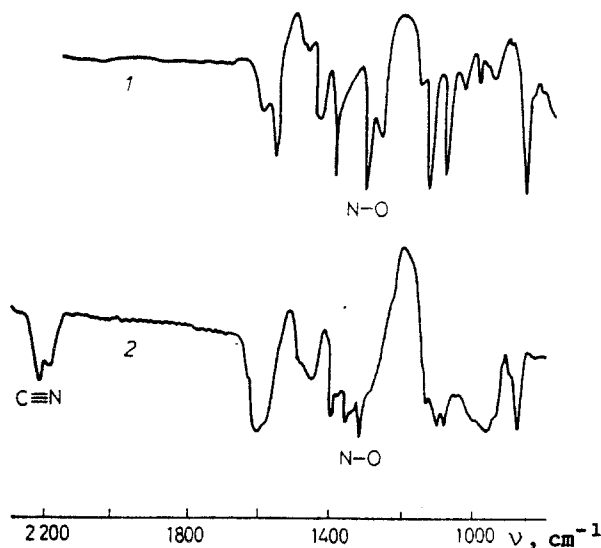
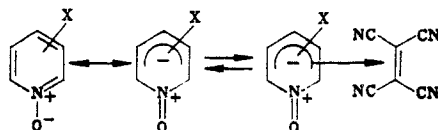


Fig. 3. IR spectra: 1) quinoline N-oxide; 2) CTC of quinoline N-oxide and TCE.

reaction center for electrons. This is consistent with the fact that the N-oxide Ia does not form a  $\pi$ -complex under these particular conditions.

In Table 2 we have listed the wavelengths of the "charge transfer" bands, extinctions, and equilibrium constants of the reaction of  $\pi$ -complexation between the N-oxide Ic and TCE in different solvents. These results indicate that the stability of the  $\pi$ -complexes decreases with increasing polarity of the solvent. In acetonitrile, formation of a  $\pi$ -complex is observed only with an 8- to 10-fold excess of TCE relative to the N-oxide. In methanol no  $\pi$ -complexation is observed. This relationship can be explained by a shift of electron density from the oxygen atom to the ring that takes place upon complexation:



As a result of diffusion of the negative charge in the  $\pi$ -complex, it becomes less solvatable than the N-oxide.

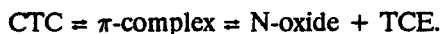
### CHARGE-TRANSFER COMPLEXES (CTCs)

Within a few hours after mixing the solutions of the N-oxides Ib-g, II, and IIIa, b, d with TCE in dioxane or THF, we observe crystallization of a solid CTC, accompanied by complete or partial decolorization (Table 3). According to the results of elemental analysis (calculation based on N content, %), the CTC composition is nonstoichiometric; it may vary slightly depending on the conditions of the experiment.

The UV spectra of the solid CTCs differ from those of the corresponding N-oxides (Fig. 1). The maxima of the  $\pi \rightarrow \pi^*$  absorption bands are shifted toward shorter wavelengths. The magnitude of the shift is directly proportional to the polarity of the solvent. The "charge transfer" bands that are characteristic for the  $\pi$ -complexes are not present in the corresponding charge-transfer complexes. This indicates a significant transfer of charge from the donor (N-oxide) to the acceptor (TCE). On the other hand, the CTCs of the N-oxides Ie, f, II, and IIIa, b, d are yellow, and this leads to the appearance of an additional band in the 390- to 430-nm region of the UV spectra.

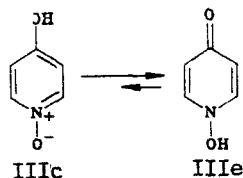
The positions of most of the absorption bands in the IR spectra (Fig. 3) of the CTCs are practically the same as in the corresponding N-oxides, but the bands of the  $\text{C}\equiv\text{N}$  bond in the CTC spectra are shifted by an average of 30-40  $\text{cm}^{-1}$  toward longer wavelengths in comparison with the TCE. This sort of relationship is always observed when TCE is bound into a CTC [5]. The vibrations of the  $\text{C}\equiv\text{N}$  bond in the TCE molecule occur in the vicinity of 2260  $\text{cm}^{-1}$ , but in the anion radical  $\text{TCE}^{\cdot-}$  in the 2210-2180  $\text{cm}^{-1}$  region. In the ESR spectra, there is no absorption, indicating strong interaction within the CTC, with the formation of a doublet ground state [6].

Upon dissolution in polar solvents (DMSO, DMFA), the CTCs partially dissociate, resulting in the appearance of the "charge transfer" bands that are characteristic for  $\pi$ -complexes:



The weakest CTC of the N-oxide Ib dissociates to a considerable degree even in chloroform. All of the CTCs are decomposed on silica gel or aluminum oxide, with quantitative formation of the original N-oxides.

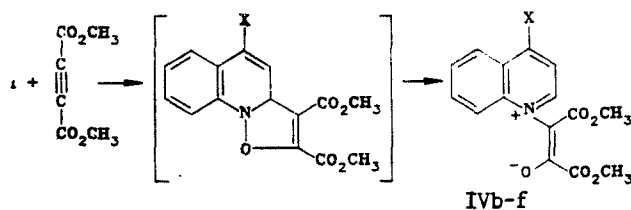
The N-oxide IIIc which, in contrast to III d, exists in the tautomeric form IIIe, does not react with TCE.



For compounds having substituents with a heteroatom, in which the unshared pair is conjugated with the system of  $\pi$ -bonds, the question of the donor center is important. In the N-oxides such centers may be the aromatic  $\pi$ -system and the oxygen of the N-oxide group; for compounds Ib, e, f and IIIa, b, d, in addition, these centers may be the chlorine, sulfur, oxygen, or nitrogen atoms of the substituents. The character of interaction of ambident donors depends on the properties of the acceptor. It is known, for example, that  $\nu$ -acids ( $\text{BF}_3$ ,  $\text{AlCl}_3$ ) react with N-oxides exclusively through the oxygen atom, forming stable  $n,\nu$ -complexes. As a result of disruption of  $p,\pi$ -conjugation of the N-oxide group with the aromatic ring, there are significant changes in the IR spectrum (vibrations of  $\text{N}^+-\text{O}^-$  bond); and the introduction of substituents in the  $\alpha$ -position lowers the reactivity of the N-oxides quite substantially as a result of steric factors [7]. In the case of TCE, the most probable is  $\pi,\pi$ -interaction since, in the first place, the vibrations of the  $\text{N}^+-\text{O}^-$  bond in the CTC correspond to the vibrations of these same bonds in the N-oxide; and, in the second place, the reaction parameters for the N-oxides Ic and Ig are very similar, indicating the absence of any steric factor. In the case of the N-oxides Ie, f and IIIa, b, d, apparently, a single, expanded  $p,\pi$ -conjugated system is formed with the participation of the unshared electron pair of the substituents. This may be the explanation for the fact that the relative content of TCE in these substituted CTCs is twice the content in the unsubstituted CTCs.

All of the CTCs are dielectrics with very similar values of the resistivity, about  $10^6 \Omega$ .

The chemical properties of the CTCs with TCE are reminiscent of the properties of the corresponding N-oxides. For example, the CTCs, like the N-oxides [8], react with the dimethyl ester of acetylenedicarboxylic acid to form betaines, obtained as a result of rearrangement of the primary cyclic adducts of 1,3-dipolar cycloaddition:



When exposed to strong acids (HCl, HBr), the CTCs decompose, forming salts of the corresponding N-oxides.

Thus, in the reaction of aromatic N-oxides with TCE, donor-acceptor interaction is the most favorable. Two kinds of molecular complexes are formed, differing in stability, degree of charge transfer, stoichiometric ratio of the components, and spectral characteristics. These complexes are classed as  $\pi,\pi$ -type complexes. The reactivity of the N-oxides correlates with the electronic properties of the substituents.

## EXPERIMENTAL

The N-oxides were synthesized by conventional procedures [9]. The TCE, manufactured by Chemapol, was recrystallized from absolute dioxane. The UV spectra were recorded in Specord M-40 and SF-26 instruments, the IR spectra (1% in  $\text{CHCl}_3$ ) in UR-20 and IKS-29 instruments, and the ESR spectra in an RÉ 1306 rf spectrometer ( $\nu$  9 Hz\*), standard 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl. The resistivity of the CTCs was measured by a four-probe method with a linear arrangement of the probes [10].

**Interaction of Quinoline N-Oxide with TCE.** A solution of 0.181 g (1 mmole) of quinoline N-oxide dihydrate in 3 ml of absolute dioxane was mixed with a solution of 0.128 g (1 mmole) of TCE in 4 ml of dioxane; the mixed solution was allowed to stand for 1 day at room temperature; then the residue was filtered off, washed with dioxane ( $2 \times 1$  ml) and ether ( $3 \times 1$  ml), air-dried, and recrystallized from a 1:1 benzene-acetone mixture. Obtained 0.138 g (51%) of the CTC.

The other CTCs were obtained analogously.

\*As in Russian original — Translator.

**Reaction of N-Oxide Ib with TCE.** This reaction was carried out for the first 24 h with cooling of the mixture to 4°C, then at room temperature. The CTC was not recrystallized, as it was unstable.

**Reaction of N-Oxide II with TCE.** This reaction was carried out in a 1:1 mixture of dioxane and benzene; the CTC was recrystallized from a 1:2 mixture of dioxane and benzene.

**Interaction of CTC of N-Oxide Ic (with TCE) with Acetylenedicarboxylic Ester.** To a solution of 0.156 g (1.1 mmoles) of the diester in 6 ml of absolute chloroform, 0.188 g (~1 mmole) of the CTC was added. The solution was mixed by means of a magnetic stirrer for 6 h at room temperature. The course of the reaction was followed by means of TLC (chloroform—ethanol, 20:1). The solution was evaporated under vacuum to a volume of 0.5 ml, and the mixture was separated in a column with 4 g of silica gel. By elution with a 20:1 mixture of chloroform and ethanol, the following fractions were obtained: dark yellow oil (products of polymerization of the acetylenedicarboxylic ester and decomposition of the TCE) 0.086 g (not identified); betaine IVc 0.107 g (38%) as a yellow powder, mp 201-202°C. Identical to known preparation obtained by interaction of N-oxide Ic with acetylenedicarboxylic ester.

**Decomposition of CTC of N-Oxide If (with TCE) by Hydrobromic Acid.** To a 0.250-g sample (~1 mmole) of the CTC in 5 ml of dioxane, 0.22 ml (~2 mmoles) of concentrated HBr was added. The colorless residue of the hydrobromide of the N-oxide If was separated by centrifuging, washed with 2 ml of dioxane and then with ether (2 × 2 ml), and recrystallized from acetone. Obtained 0.204 g (76%) of the salt, mp 146-148°C. Identical to a known salt obtained by the interaction of the N-oxide If with HBr.

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#### SYNTHESIS OF SUBSTITUTED 2-HYDRAZINO- AND 2-( $\beta$ -ACYLHYDRAZINO)-CINCHONINIC ACID AMIDES AND THEIR CYCLIZATION TO 1,2,4-TRIAZOLO[4,3-*a*]QUINOLINE-9-CARBOXYLIC ACID AMIDES

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UDC 547.832

*The reaction of substituted 2-chlorocinchoninic acid amides with hydrazine hydrate or acylhydrazines gave 2-hydrazino- and 2-( $\beta$ -acylhydrazino)cinchoninic acid amides. The latter were also obtained by acylation of the 2-hydrazino derivatives. It is shown that 1,2,4-triazolo[4,3-*a*]quinoline-9-carboxylic acid amides are formed when 2-hydrazinocinchoninic acid amides are refluxed with formic or acetic acid.*

2-Hydrazinocinchoninic acid amides have not been previously investigated. At the same time, they are of interest as starting compounds for obtaining condensed heterocycles containing a quinoline fragment and as potentially biologically active substances [1].