π–π Molecular Complexes with Nitrones, II[1].
Complexation Between Heterocyclic Nitrones and Tetracyanoethylene as well as 1,4-Benzoquinones

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Characteristic charge-transfer absorption bands of some heterocyclic nitrones as electron donor with tetracyanoethylene, 2,3-dichloro-5,6-dicyanobenzoquinone and chloranil as electron acceptor have been measured in methylene chloride solution. The stoichiometry, apparent formation constants and transition energies of the charge-transfer complexes formed as well as the effect of solvent and the stability of these complexes are discussed.

(Keywords: Charge transfer absorption bands; Nitrones)

π—π-Molekülkomplexe von Nitronen, 2. Mitt.: Komplexe zwischen heterocyclischen Nitronen und Tetracyanoethylen bzw. 1,4-Benzochinonen

Die charakteristischen Charge-Transfer Absorptionen einiger heterocyclischer Nitrone als Elektron-Donor mit Tetracyanoethylen, 2,3-Dichlor-5,6-dicyanobenzochinon bzw. Chloranil als Elektron-Acceptor wurden in Methylenchlorid als Lösungsmittel gemessen. Stöchiometrie, effektive Bildungskonstanten und Einfluß des Lösungsmittels auf die Stabilität der Komplexe werden diskutiert.

Introduction

The π-base strength of the electron donor as well as the π-acid strength of the electron acceptor can be measured from studies on their charge-transfer complexes[1–10]. Furthermore, the activity of some biologically active compounds may depend on their tendency to form such molecular complexes with biological receptors[11a,b]. Charge-transfer complexes between heteroaromatic five membered ring compounds[9],

substituted indoles[10] and tetracyanoethylene (*TCNE*) have been studied. The acceptor character of 1,4-benzoquinones carrying different electronegative substituents was established from studies of their molecular complexes with aromatic hydrocarbons[7]. Recently the intermolecular charge-transfer complexes of some arylnitrones as electron donor, with *TCNE*, 2,3-dichloro-5,6-dicyanobenzoquinone (*DDQ*) and chloranil (*CHL*) as electron acceptor, have been studied and the constitution of the complexes formed has been determined[1]. In conti-
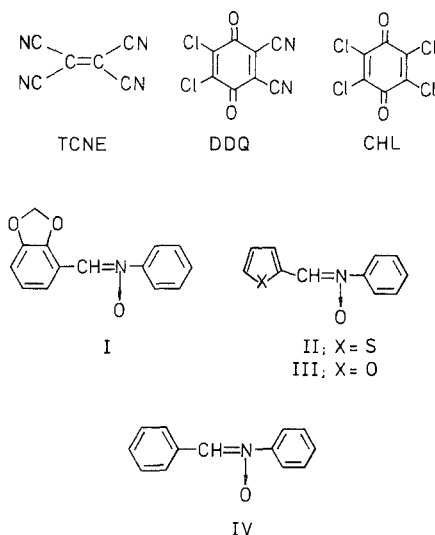

Fig. 1

nuation of our work on the charge-transfer complexes between nitrones and *TCNE* as well as 1,4-benzoquinones, we wish now to discuss the probability of formation of such complexes with heterocyclic nitrones (I-III) and also to investigate the role of the heterocyclic part of the nitrones in complex formation.

Experimental

TCNE (Fluka AG purum) was recrystallised from chlorobenzene and sublimed, *DDQ* and *CHL* (Aldrich) were sublimed. The nitrones I-III were prepared by the recommended methods[12a, b]. The purity of all samples was shown to be better than 99.8% by v.p.c. Methylene chloride, benzene, cyclohexane, diethyl ether, ethyl acetate and acetone were purified according

to *Vogel*[13a] and *Organicum*[13b], dried and distilled. $3 \cdot 10^{-2}\,M$ stock solutions of each of the nitrones (I–III), *TCNE*, *DDQ* and *CHL* were prepared by dissolving the accurately weighed amounts of each compound in the organic solvent. The spectral measurements were carried out within a few minutes after mixing both donor and acceptor solutions, since on standing the obtained coloured solutions become more deeper, although the positions of all $\lambda_{\max}$ remain unchanged.

All absorption spectra measurements were made with a Beckman spectrophotometer model 26, using 3.5 cm cell.

Results and Discussions

The physical data of the charge-transfer complexes of the nitrones I–III with *DDQ* and *TCNE* are reported in Table 1. The maximum absorption wavelengths of the complexes formed were measured in methylene chloride at 25 °C. On addition of *CHL* to each of the nitrones under examination yellow coloured solutions were observed giving no band characteristics for charge-transfer complexes. This behaviour may be due to the low electron affinity value of *CHL* (1.37 eV) in comparison with the relative higher affinity values of *TCNE* and *DDQ* (1.68 and 1.91 eV, respectively)[14]. Similar results have been observed in complexation between *CHL* and different arylnitrones[1].

The molecular complexes obtained from complexation between the nitrones I–III and *TCNE* gave bands in the 555–585 nm region, however in case of the *DDQ* complexes the absorptions lie in the 635–685 nm region. The absorption bands in these two regions are ascribed to the formed complexes, since neither the nitrones I–III nor the acceptors (*TCNE* or *DDQ*) alone absorb in these regions. The $\lambda_{\max}$ of the nitrone—*TCNE* and —*DDQ* complex varies with the structure of the heterocyclic part of the nitrones studied (cf. Table 1). In a previous communication we reported the absorption spectra of diphenyl nitrone complexes IV—*TCNE* and IV—*DDQ*, which absorb at $\lambda_{\max}$ 535 and 575 nm respectively[1]. Comparing the $\lambda_{\max}$ of the complexes of the two nitrones II and III in Table 1 with that of IV it was shown that the absorption of the two heterocyclic nitrones II and III has been shifted to longer wavelength. Accordingly, it may be concluded that both II and III are more basic than IV, wich might be ascribed to both electronic and mesomeric effects of the heterocyclic part of the nitrone. Furthermore, the positive charge left on the π-base after electron transfer to the electron acceptor is expected to be more stabilized in case of the heterocyclic nitrones. The high π-base character of the third nitrone under investigation (I) may be due to the presence of two oxygen atoms in conjugation with the benzene ring.

$\lambda_{\max}$, the apparent formation constants K_f and the transition energy values E for the complexes of nitrones with *TCNE* and *DDQ* are

Table 1. *Maximum absorption wavelengths* λ_{max} (nm), *molar extinction coefficients* ϵ_{max} (mol^{-1} cm^2), *apparent formation constants* K_f *and transition energies* E (kcal/mol) *for the absorption bands of charge-transfer complexes formed between the nitrones I-III and TCNE or DDQ in methylene chloride at 25 °C*

Electron donor	Electron acceptor	λ_{max}	ϵ_{max}	K_f	E
I	*TCNE*	585	56	$6.40 \cdot 10^4$	48.88
II	*TCNE*	560	67	$5.19 \cdot 10^4$	51.07
III	*TCNE*	555	42	$5.11 \cdot 10^4$	51.53
I	*DDQ*	685	30	$5.18 \cdot 10^4$	41.75
II	*DDQ*	640	53	$4.60 \cdot 10^4$	44.68
III	*DDQ*	635	31	$3.19 \cdot 10^4$	45.03

in general agreement with the corresponding electron donor and acceptor characters. The λ_{max} and K_f values increase in the same order of increasing the π-base character of nitrones (I > II > III) and the π-acid character of the acceptors (*DDQ* > *TCNE* > *CHL*).

The stoichiometry of the molecular complexes studied were determined by applying two methods[15,16]: (i) The conventional spectrophotometric molar ratio method. In this method a series of solutions was prepared in which the concentration of the π-base is kept constant while
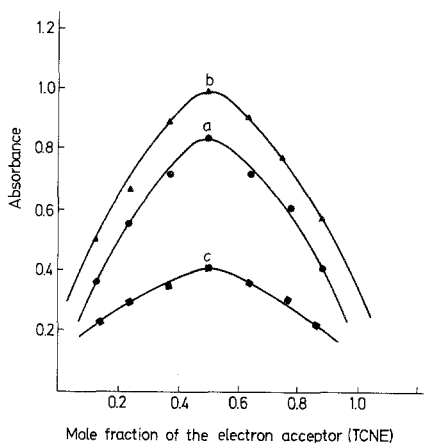

Fig. 2. Continuous variation method for the molecular complexes: *a TCNE* + I; λ_{max} = 585 nm, total concentration = $3 \cdot 10^{-2}$ mol; *b TCNE* + II; λ_{max} = 560 nm, total concentration = $3 \cdot 10^{-2}$ mol; *c TCNE* + III; λ_{max} = 555 nm, total concentration = $2 \cdot 10^{-2}$ mol. Solvent: methylene chloride
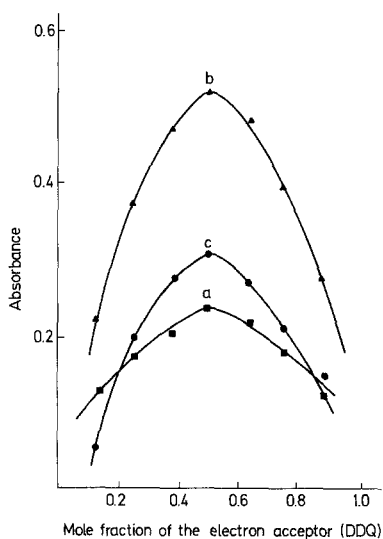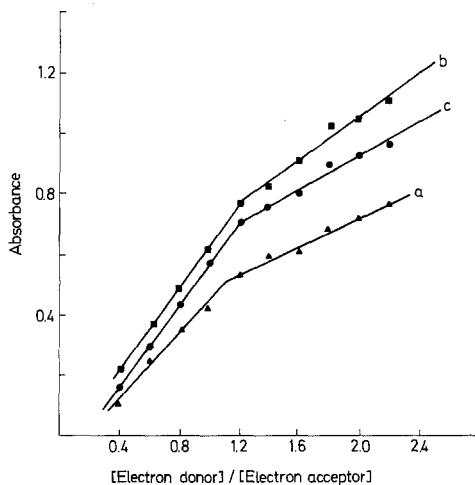
Fig. 3. Continuous variation method for the molecular complexes: a $DDQ + \mathrm{I}$; $\lambda_{\max} = 685\,\mathrm{nm}$, total concentration $= 2 \cdot 10^{-2}\,\mathrm{mol}$; b $DDQ + \mathrm{II}$; $\lambda_{\max} = 640\,\mathrm{nm}$, total concentration $= 2 \cdot 10^{-2}\,\mathrm{mol}$; c $DDQ + \mathrm{III}$; $\lambda_{\max} = 635\,\mathrm{nm}$, total concentration $= 1.5 \cdot 10^{-2}\,\mathrm{mol}$. Solvent: methylene chloride

Fig. 4. Molar ratio method for complexes: a $TCNE + \mathrm{I}$; $\lambda_{\max} = 585\,\mathrm{nm}$, total concentration $= 3 \cdot 10^{-2}\,\mathrm{mol}$; b $TCNE + \mathrm{II}$; $\lambda_{\max} = 560\,\mathrm{nm}$, total concentration $= 3 \cdot 10^{-2}\,\mathrm{mol}$; c $TCNE + \mathrm{III}$; $\lambda_{\max} = 555\,\mathrm{nm}$, total concentration $= 2 \cdot 10^{-2}\,\mathrm{mol}$. Solvent: methylene chloride

that of the π-acid is varied to cover the molar ratio [π-base]:[π-acid] from 0.25 to 3.0. (ii) The continuous variation method. In this method a series of solutions was prepared in which the concentration of both the π-base and π-acid components is varied while the total molar concentration of the two components is kept constant. The electronic spectra of all solutions prepared were recorded within the wavelength range 200-750 nm, using methylene chloride as a solvent and as a blank. The continuous variation method was used in complexation between the nitrones I–III and both $TCNE$ and DDQ, however the molar ratio method was used in complexation with $TCNE$. The results obtained reveal that the stoichiometric ratio of the different complexes studied is 1:1. Representative results are shown in Figs. 2, 3 and 4. The apparent formation constants (K_f) of the molecular complexes formed were determined from the continuous variation curves by making use of the following equation, which was previously applied in metal complexes: $K_f = (A/A_m)/C \cdot (1 - A/A_m)^2$, where A_m is the limiting absorbance corresponding to the maximum formation of the complex and A is the absorbance at electron donor concentration C.

Solvent Effects

A number of investigators[17] have been studied solvent effects on the electronic absorption spectra of the intermolecular charge-transfer complexes. The maximum absorption wavelength of II—$TCNE$ complex was measured in a number of solvents. Table 2 lists the results obtained, demonstrating that the position of the maximum absorption wavelength of the II—$TCNE$ complex varies as much as 60 nm. The behaviour of the heterocyclic molecular complex II—$TCNE$ in different solvents (Table 2) is similar to that of aryl nitrones[1]. In case of the oxygenated solvents no correlation appears between the polarity of the

Table 2. *Effect of solvent on position of the maximum wavelength band of the II—TCNE complex in different organic solvents at 25 °C*

Solvent	λ_{max} (nm)	ϵ_{max} (mol^{-1} cm^2)	E kcal/mol	Dielectric constant[18] at 25 °C
Methylene chloride	560	67	51.07	9.1
Benzene	552	82	51.81	2.3
Cyclohexane	545	23	52.47	2.0
Diethylether	540	120	52.96	4.3
Ethylacetate	515	31	55.53	6.0
Acetone	500	73	57.19	20.7

solvent and the transition energy. This is attributed to the complexation between the solvent itself and $TCNE^2$. On the other hand, in case of nonoxygenated solvents the transition energy of the molecular complex decreases as the polarity of the solvent is increased. The role of the polarity of the solvents arises from the stabilization of the excited state of the molecular complex through dipole-dipole or dipole-induced dipole interactions. Accordingly, the transition energy of the molecular complex is inversly proportional to the polarity of the nonoxygenated solvent.

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