Charge Transfer Complexes of N-Arylcarbamates with π-Acceptors

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The charge-transfer (CT) complexes of some N-arylcarbamates as donors with a number of π-acceptors have been studied spectrophotometrically. The Lewis basicities of the N-arylcarbamates as well as the types of interactions are discussed. The ^{1}H-NMR spectra of some CT complexes with both 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) indicate a decrease of the electron density on the donor part of the complex.

1. Introduction

Some investigators [1, 2] have suggested that the activity of biologically active compounds may be due to their abilities to form CT complexes with biologically active receptors. It has been reported that the basic esters of phenylcarbamic acid belong to the group compounds with considerable local anesthetic and antiarythmic activities [3–5]. In a recent study, the CT complexes of some phenylcarbamates possessing local anesthetic activity (1-[2-alkoxyphenylcarbamoyloxy)ethyl]-piperidinium chloride) as electron donors with chloranil (CHL) as π-acceptor have been investigated [6].

In the present work I wish to report the CT complexation of several substituted N-arylcarbamates, which belong to the mentioned class of compounds, with a number of π-acceptors with the aim to investigate the apparently weak electron donating behaviour of this interesting donor system. Beside the spectrophotometric study of the CT complexes, the ^{1}H-NMR spectra of some CT complexes are discussed in order to confirm the CT transitions.

Numerical values of the association constants (K) and molar extinction coefficients (ε) for the CT complexes studied are computed by using the Rose-Drago equation [7, 8] which is considered as a most reliable method and which is perfectly general.

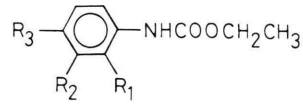
2. Experimental and Physical Measurements

N-Arylcarbamates I–II (Fig. 1) were prepared according to references [9] and [10].

Tetracyanoethylene (Janssen Chimica, Belgium), 2,3-dichloro-5,6-dicyanobenzoquinone, chloranil, bromanil (BRL) (Merck, Federal Republic of Germany) and 7,7,8,8-tetracyanoquinodimethane (EGA-Chemie, F. R. Germany) were used without further purification.

Methylene chloride (Merck) was dried over phosphorus pentoxide and distilled following reference [11].

The association constants of formation (K) and molar extinction coefficients (ε) of the CT com-



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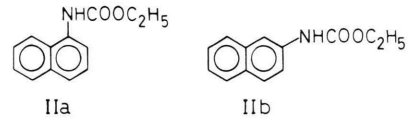
a) $R_1 = R_2 = H$; $R_3 = OCH_3$
b) $R_2 = R_3 = H$; $R_1 = OCH_3$
c) $R_1 = R_3 = H$; $R_2 = OCH_3$
d) $R_1 = R_2 = H$; $R_3 = CH_3$
e) $R_2 = R_3 = H$; $R_1 = CH_3$
f) $R_1 = R_3 = H$; $R_2 = CH_3$
g) $R_1 = R_2 = R_3 = H$
h) $R_1 = R_2 = H$; $R_3 = Cl$
i) $R_1 = R_2 = H$; $R_3 = NO_2$



IIa IIb

Fig. 1

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plexes studied have been determined by applying the Rose-Drago equation [7, 8]:

$$K^{-1} = \frac{C_D C_A(\varepsilon - \varepsilon_A)}{d - d_A} - C_D - C_A + \frac{d - d_A}{\varepsilon - \varepsilon_A},$$

where C_D and C_A are the initial concentrations of the donor and acceptor, respectively, ε_A is the molar absorbtivity of the acceptor, d_A is the absorbance of the initial concentration of the acceptor, and d corresponds to the total absorbance at any given wavelength for a cell of 1 cm path length.

The visible spectra were determined on a Beckman 26 recording spectrophotometer in a matched pair of stoppered fused silica cells of 1 cm optical path length. All scans covered the range from 350 to 800 nm. Optical measurements were made up as soon as possible after the solutions were prepared.

The ^{1}H-NMR [12] spectra of donors and their corresponding CT complexes were determined by using concentrated solutions of donors and acceptors in $CDCl_3$ with tetramethylsilane as internal standard and recorded on a Varian T-60 (60 MHz) spectrometer.

3. Results and Discussion

Taking into consideration the presence of an electron withdrawing ester group in the electron donor system under examination, it may be concluded that this class of compounds is weakly electron donating. However, on mixing the methylene chloride solutions of the donors I–II and acceptors (Fig. 1), different colours characteristic of CT transitions were observed. This fact was further supported by measurement of the absorption of these solutions, which gave CT characteristic broad bands that absorbed in the visible region, in which neither the donor nor the acceptor separately absorb.

Table 1 includes the wavelengths of the maximum absorption of the CT complexes between N-arylcarbamates I–II and the π-acceptors; DDQ, TCNE, TCNQ, CHL and BRL. As seen from this Table, the CT complexes of the donors I–II with TCNE exhibit two maxima in the region 371–617 nm, however the other CT complexes are characterized by a single CT transition within the range 557–729 nm. The absorption of the CT complexes at double maxima can reasonably be explained as due to electron transfer from the two highest occupied molecular orbitals of the electron donor to the lowest vacant molecular orbital of the acceptor.

On the basis of the CT absorption maxima of the CT complexes in Table 1, the electron affinities of the electron acceptors utilized in this paper must decrease in the following order: DDQ > TCNQ > TCNE > CHL > BRL. On the other hand, according to the reported electron affinity values of these π-acceptors [13], this order should be as follows: DDQ > TCNE > TCNQ > CHL > BRL. Comparison of the association constants of the CT complexes in Table 2 reveals an excellant fit for the last order. Consequently, the K values of the CT complexes of a series of donors with different acceptors could be used as a measure of the electron affinities of the acceptors rather than the values of wavelengths of maximum absorption.

Analysis of the data in Table 1 indicates that the electron donors Ia–h are arranged in an order of decreasing ability to release electrons to the π-acceptors. The long wavelength maxima of the CT complexes of N-anisylcarbamates with the π-acceptors confirm the expected order of decreasing the

Table 1. Charge-transfer absorption maxima of the CT complexes studied (nm).

Carbamate	DDQ	TCNE	TCNQ	CHL	BRL
Ethyl N-p-anisylcarbamate (Ia)	729	371, 614	660	591	590
Ethyl N-o-anisylcarbamate (Ib)	675	417, 587	585	515 (sh)	–
Ethyl N-m-anisylcarbamate (Ic)	625 (sh)	417, 550 (sh)	525 (sh)	–	–
Ethyl N-p-tolylcarbamte (Id)	636	387, 572	557	495 (sh)	480 (sh)
Ethyl N-o-tolylcarbamate (Ie)	588	412, 517 (sh)	500 (sh)	–	–
Ethyl N-m-tolylcarbamate (If)	603	412, 525 (sh)	525 (sh)	–	–
Ethyl N-phenylcarbamate (Ig)	577	382, 500 (sh)	480 (sh)	–	–
Ethyl N-p-chlorophenylcarbamate (Ih)	550 (sh)	462, 500 (sh)	480 (sh)	–	–
Ethyl N-α-naphthylcarbamate (IIa)	710	413, 595	612	511 (sh)	–
Ethyl N-β-naphthylcarbamate (IIb)	705	412, 600	607	520 (sh)	520 (sh)

Table 2. Values of molar extinction coefficients (ε), association constants (K), transition energies (E), oscillator strengths (f) and transition dipole moments (μ) of the CT complexes studied.

Donor	Acceptor	ε ($l \cdot mol^{-1} cm^{-1}$)	K ($l \cdot mol^{-1}$)	E (e. V.)	f	μ (D)
Ia	DDQ	66	33.75	1.71	0.039	2.05
Ib	DDQ	80	30.57	1.84	0.028	1.99
Id	DDQ	90	26.99	1.96	0.025	1.77
Ie	DDQ	35	17.55	2.11	0.020	1.66
If	DDQ	60	23.05	2.06	0.005	2.77
Ig	DDQ	46	20.03	2.15	0.036	1.71
IIa	DDQ	15	30.34	1.75	0.061	2.77
IIb	DDQ	35	13.67	1.75	0.040	2.21
Ia	TCNE	40	11.63	3.35, 2.03	0.052	2.77
Ib	TCNE	42	6.52	2.98, 2.12	0.039	2.13
Id	TCNE	90	5.59	3.21, 2.17	0.018	1.51
IIa	TCNE	70	17.17	3.01, 2.09	0.046	0.66
IIb	TCNE	90	12.16	3.02, 2.07	0.024	1.76
Ia	TCNQ	60	2.85	1.88	0.032	1.94
Ib	TCNQ	200	1.55	2.13	0.017	1.56
Id	TCNQ	55	2.10	2.23	0.012	1.45
IIa	TCNQ	40	3.81	2.03	0.019	1.58
IIb	TCNQ	11	11.99	2.05	0.005	0.83
Ia	CHL	105	4.82	2.13	0.029	2.02
Ia	BRL	85	4.15	2.11	0.010	1.23

base strength; p-anisyl (Ia) > o-anisyl (Ib) > m-anisyl (Ic); however in case of the CT complexes of N-tolylcarbamates (Id–f) the order of decreasing basicity of the three isomers is as follows: p-tolyl (Id) > m-tolyl (If) > o-tolyl (Ie). It is noteworthy that the relatively high basicity of the m-tolyl isomer with respect to the o-tolyl isomer is due to the fact that the o-isomer is more sterically hindered than the m-isomer. In addition, in case of the N-anisylcarbamates the mesomeric effect of the o-methoxyl group is more effective than its steric effect. The strong electron withdrawing and inductive effects of the nitro group in p-nitrophenylcarbamate (Ii) tend to decrease its donor ability so that it does not form CT complexes with any of the π-acceptors.

The data in Table 1 show also that the donor character of N-naphthylcarbamates lies between those of N-para and N-o-anisylcarbamates. In other words, the electron releasing effect of the methoxyl group and the effect of the extra fused benzene ring in II are comparable in magnitude.

Values of the association constant (K) for the CT complexes together with the molar extinction coefficients (ε) were determined by again making use of the Rose-Drago equation [7, 8] and are shown in Table 2. From the data in Tables 1 and 2 it is noticeable that both the λ_{max} and K values nearly follow the same order. However the λ_{max} values did not follow the same sequence as the corresponding molar extinction coefficients. The steric requirements in the donor system are responsible for this behaviour.

The energy of the CT transitions (E) reported in Table 2 have been calculated by using Briegleb's equation [14]. Further information about the relative basicities of the donor under investigation could be inferred from the E values.

The oscillator strength (f) and the transition dipole moment (μ) of the CT complexes presented in Table 2 were computed from the following approximated equations [15, 16]:

$$f = 4.32 \times 10^{-9}\, \varepsilon_{max} \cdot \nu_{1/2}\,,$$

$$\mu = 0.0958\, [\varepsilon_{max} \cdot \nu_{1/2}/\nu_{max}]^{1/2}\,,$$

where ε_{max} is the molar absorbance at the CT maximum, ν_{max} is the frequency of the CT maximum in cm^{-1} and $\nu_{1/2}$ is the half width in cm^{-1}.

It is well known that both the f and μ values of given complexes increase with decreasing base strength of the corresponding donors. In the present work, the data in Table 2 reveal no regular correlation. This may stem from structural factors of both donors and acceptors.

Table 3. ^{1}H-NMR spectra of the CT complexes of donors Ia, d, e, IIa, b with DDQ and TCNQ ($CDCl_3$, δ, TMS).

Free donor and complex	NH	Ar–H	CH_2, CH_3	others
Ia	6.70	7.08	4.23, 1.30	OCH_3; 3.73
Ia-DDQ	6.87	7.12	4.24, 1.31	OCH_3; 3.75
Ia-TCNQ	6.86	7.12	4.24, 1.30	OCH_3; 3.75
Id	6.67	7.23	4.27, 1.30	CH_3; 2.30
Id-DDQ	6.74	7.24	4.27, 1.31	CH_3; 2.32
Id-TCNQ	6.73	7.24	4.28, 1.32	CH_3; 2.31
Ie	6.38	7.63–7.08	4.26, 1.30	CH_3; 2.30
Ie-DDQ	6.57	7.65–7.10	4.27, 1.32	CH_3; 2.32
Ie-TCNQ	6.50	7.65–7.09	4.26, 1.31	CH_3; 2.31
IIa	7.00	8.17–7.37	4.30, 1.33	–
IIa-DDQ	7.23	8.18–7.42	4.32, 1.34	–
IIa-TCNQ	7.17	8.17–7.42	4.32, 1.34	–
IIb	6.97	8.07–7.22	4.27, 1.27	–
IIb-DDQ	7.13	8.13–7.25	4.29, 1.29	–
IIb-TCNQ	7.08	8.12–7.27	4.28, 1.28	–

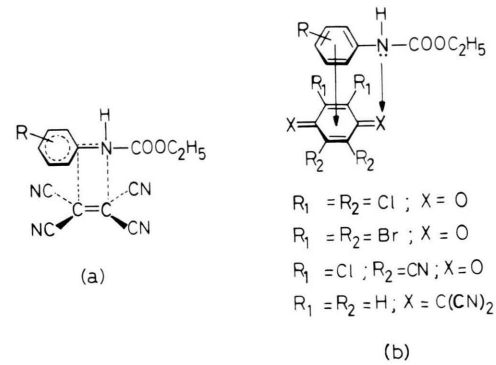

Fig. 2

as one in which the C–C double bond of TCNE lies on the N-aryl bond in which the electron density is more concentrated because of the electron delocalization between the lone pair of the nitrogen atom with the aryl group. As a result, both $n-\pi^*$ and $\pi-\pi^*$ transitions are possible (Fig. 2a); (ii) in case of the CT complexes of substituted p-benzoquinones and TCNQ, the aryl group of the donor lies on the nucleus of the acceptor and the nitrogen atom lies on the oxygen atom of DDQ, CHL, BRL and on $C(CN)_2$ in case of TCNQ. Consequently, both $n-\pi^*$ and $\pi-\pi^*$ CT transitions may exist (Fig. 2b) and the broadness of the CT bands may arise from overlapping of two maxima due to different transitions.

The ^{1}H-NMR spectra of the CT complexes of donors Ia, d, e, IIa, b with both DDQ and TCNQ were determined. Comparison of the chemical shift of the NH proton for the free electron donors with their corresponding complexes (Table 3) reveals a marked shift to lower field for the NH protons of the CT complexes, indicating a decrease of the electron density on the donor molecule.

Taking into consideration that the nitrogen atom would be the centre contributing to the intermolecular CT interaction, the type of transitions between the donors I–II and the π-acceptors could be explained as follows: (i) in case of the CT complexes with TCNE, there is an electron transfer from the HOMO of the N-aryl to the LUMO of TCNE, and the CT complex may be designated

Application of Job's method [17] of continuous variation gave symmetrical curves with maxima at a mole fraction 0.5 indicating a 1:1 stoichiometric ratio. Also, the association constants calculated at both peaks in the CT complexes with TCNE are in good agreement with each other in all cases, indicating that the two CT bands are due to the 1:1 complex.

In a recent study [18] it has been found that the CT complexes of p-methoxyacetanilide with both DDQ and TCNE absorb at λ_{max} 576 and 605 nm, respectively. Comparison of λ_{max}'s of the CT complexes of ethyl N-p-anisylcarbamate (Ia) with DDQ and TCNE with those of its analogue, p-methoxyacetanilide, with the same acceptors reveals that the former is more basic than the latter. That is to say that the mesomeric effect of the OC_2H_5 group in the carbamate molecule is more effective than the inductive effect of the CH_3 group in $COCH_3$ of the acetanilide.

On conclusion, the donors under investigation have proven to be highly electron donating systems. This fact has been supported from the study of the ^{1}H-NMR spectra of the CT complexes as well as the high blue shift of their CT complexes relative to their corresponding acetanilide analogue.

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