

STUDIES OF INTER- AND INTRA-MOLECULAR
DONOR-ACCEPTOR INTERACTIONS - VII

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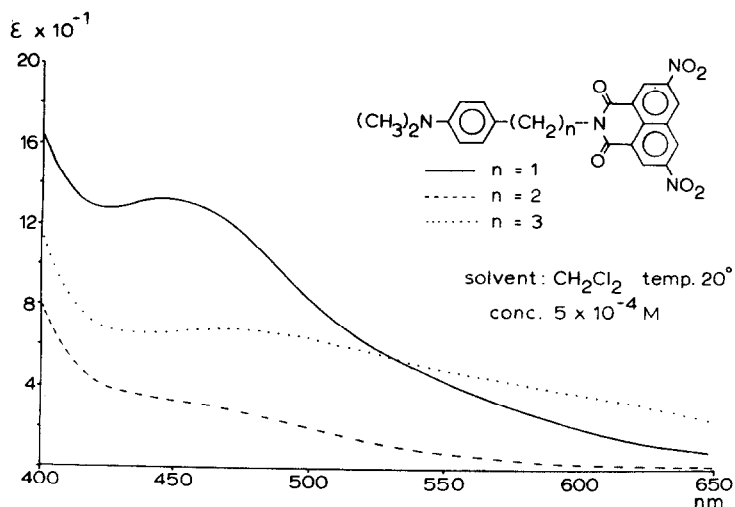
Introduction

In previous papers (1-6) we have shown, that intramolecular charge transfer (CT) interaction can occur in systems $D-(CH_2)_n-A$, in which D is a neutral aromatic electron-donor and A is a positively charged electron-accepting substituted pyridinium group. The spectra of these systems show an intramolecular CT transition resulting from interaction between D and A. The intensity of this CT transition was found to be considerably higher for $n=1$ and 2 than for $n=3$ and 4. There are indications (7-11) that intramolecular CT interaction may also occur in systems where A is a neutral acceptor. In nearly all these cases the intramolecular CT transition is strongly overlapped by the absorptions of the separate D and A chromophores, which makes quantitative conclusions very doubtful.

We now for the first time wish to report our results on a system in which intramolecular interaction between a neutral electron-donor and a neutral electron-acceptor leads to the observation of a discrete intramolecular CT transition. It will be shown that the intensity of this CT transition depends again on the length of the aliphatic chain (value of n) but in a different manner than for the charged pyridinium analogous.

Results and discussion

In the figure the absorption spectra of compounds I, II and III ($n=1, 2$ and 3 resp.) are shown.



These systems contain the *N,N*-dimethylaminophenyl system as an electron-donor and the 3,6-dinitro-(1,8)-naphthalic imide group as an electron-acceptor.

Table 1

Position and intensity of inter- and intra-molecular CT transitions in CH_2Cl_2 at 20° .

Compound	λ_{max} (nm)	ϵ_{max}	$(\epsilon_{\text{max}}^{1\text{cm}})$
I	444.5 ± 1	132	
II	-	-	
III	467	68	
$\text{C}_6\text{H}_5\text{NMe}_2 (5 \cdot 10^{-2}\text{M})$ with IV (10^{-2}M)	506		(0.31)

In Table 1 the longwavelength absorption maxima observed in the spectra of I, II and III are compiled. These maxima are attributed to an intra-molecular CT transition because, (i) Beer's law is followed, (ii) there is an inter-molecular CT transition in the same wavelength region for a solution containing *N,N*-dimethylaniline and *N*-ethyl-3,6-dinitro-(1,8)-

naphthalic imide (IV), (cf. Table 1). In contrast with our results for the systems containing a charged acceptor we now observe a maximum CT intensity for $n=1$ and 3 , while for $n=2$ no maximum is found.

These results indicate that the occurrence of an intramolecular CT transition in systems containing a neutral donor and acceptor requires another orientation of the donor towards the acceptor, than in systems where the acceptor is a charged group. Model studies show that especially in III a parallel orientation of donor and acceptor may be responsible for the occurrence of the intramolecular CT interaction. A detailed discussion on these and other systems showing intramolecular CT interaction will be given in further papers (12).

Experimental

The synthesis of compounds I, II and III will be described elsewhere (12). UV absorption spectra were measured in methylene chloride (UVASOL-Merck) at 20° with a Cary model 14 recording spectrophotometer, using cells of 1 and 10 cm pathlength.

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