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INTRAMOLECULAR CHARGE-TRANSFER INTERACTION IN SUBSTITUTED BENZYL PHENYL SULFONES

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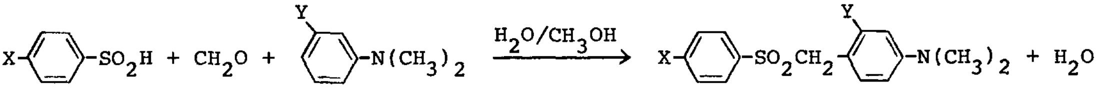
Intramolecular charge-transfer (CT) interaction involving an uncharged electron donor (D) and an uncharged electron acceptor (A) has been rarely observed.[1-3] Usually the CT interaction is weak and no discrete CT maximum can be observed in the ultraviolet or visible region.

In this communication we report the first examples of intramolecular CT interaction in two substituted benzyl phenyl sulfones $D-CH_2SO_2-A$. These sulfones[4] were prepared as part of our continuing study[5,6] of the condensation reactions of sulfinic acids with aldehydes and nitrogen bases or active C-H compounds.[7]



Ia-Ic

In fig. 1 the UV spectra of Ia ($X = NO_2$, $Y = O\overset{\overset{O}{\|}}{C}NH(CH_3)$; orange crystals; m.p. 168-169°), Ib ($X = NO_2$, Y = H; orange crystals; m.p. 200-201°) and Ic[8] ($X = CH_3$, Y = H; colourless) are given as well as that of methyl p-nitrophenyl sulfone (II) for comparison.

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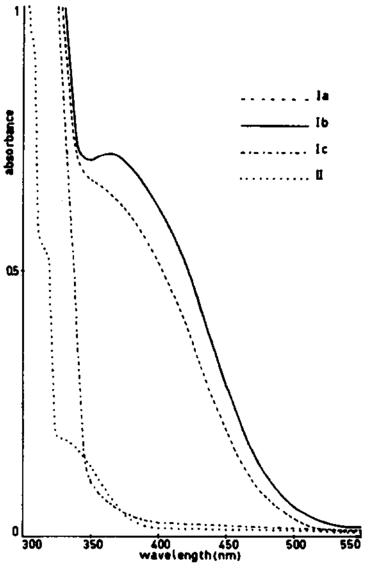

Fig. 1. UV spectra of Ia-Ic and II (10^{-3} M in $CHCl_3$).

The absorption maxima in the longer wavelength region ($\lambda > 300$ nm) observed for Ia ($\lambda_{max}^{CHCl_3}$ ca. 355 nm, ε 460 $l.mole^{-1}.cm^{-1}$; λ_{max}^{EtOH} ca. 346 nm, ε 650 $l.mole^{-1}.cm^{-1}$) and Ib ($\lambda_{max}^{CHCl_3}$ 364 nm, ε 530 $l.mole^{-1}.cm^{-1}$) cannot be attributed to either of the separate chromophores. Since Beer's law is obeyed in the concentration range between at least 10^{-4} and 2.10^{-2} M, we assume that intramolecular CT interactions are involved between the (substituted) N,N-dimethyl-p-toluidine group as electron donor and the p-nitrophenylsulfonyl moiety as electron acceptor. Apparently, sulfones of type I can adopt folded conformations that allow for efficient overlap between the π-electron systems of D and A. This is confirmed by NMR measurements on Ia-Ic (Table 1). The aromatic proton absorptions of both D and A show appreciable upfield shifts (as compared with the separate moieties of suitable reference compounds) indicating the close proximity of the D and A aromatic rings. The upfield shifts are definitely not the result of intermolecular interactions, because they remain unchanged upon variation of the solute concentration between 2.10^{-2} and 10^{-1} M.

Table 1

Chemical shifts[a] of the aromatic protons of the D and A groups of Ia-Ic and of suitable reference compounds (0.02 M in $CDCl_3$).

Compound	A		D	
	$\delta_{H_{2,6}}$	$\delta_{H_{3,5}}$	$\delta_{H_{2,6}}$	$\delta_{H_{3,5}}$
Ia	7.81	8.23	6.93 (1H)[b,c]	~6.40
Ib	7.77	8.23	6.88	6.54
Ic	7.52	7.22	6.93	6.62
$\underline{p}$-$NO_2C_6H_4SO_2CH_3$ (II)	7.92	8.41		
$\underline{p}$-$CH_3C_6H_4SO_2CH_3$	7.79	7.34		
$\underline{p}$-$(CH_3)_2NC_6H_4CH_3$ (III)			7.05	6.81

[a] Determined on a Varian A-60 D instrument using an audio oscillator side band technique. Chemical shifts in ppm relative to TMS (δ= 0).

[b] δ_{H_6}.

[c] $\underline{m}$-$(CH_3)_2NC_6H_4OC(O)NH(CH_3)$: $\delta_{H_{2,4,6}}$ 6.50 ppm (3H), centre of multiplet, δ_{H_5} 7.10 ppm (1H), centre of multiplet.

At the moment no definite conclusions can be drawn concerning the mole fractions of Ia-Ic that exist in folded conformations. However, in conformations such as depicted in fig. 2 intramolecular CT interaction might be facilitated by the known preference[9] of phenyl sulfones to exist in conformations in which the ring C-1 2$\underline{p}$-orbital is staggered between the two sulfonyl oxygen atoms.[10]

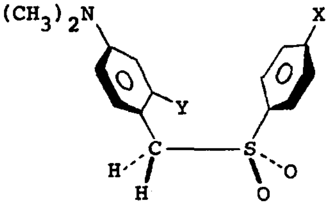

Fig. 2

Intermolecular CT interaction between N,N-dimethyl-p-toluidine (III) and methyl p-nitrophenyl sulfone (II) in chloroform solution could only be detected using high donor concentrations (i.e. III, 3M + II, 10^{-3} M; $\lambda_{max}^{CHCl_3}$ 435 nm). It is significant to note that the intermolecular CT transition is found at a longer wavelength than in the case of intramolecular CT (Ib). This is likely caused by the shorter average distance between the interacting chromophores.[11]

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