

HYDROGEN ISOTOPE EFFECTS IN ELECTRON DONOR-ACCEPTOR SYSTEMS

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Abstract: The charge-transfer (CT) transition of complexes involving alkylated aromatic electron donors shifts hypsochromically upon benzylic deuteration. This is attributed to hyperconjugative effects.

The study of hydrogen isotope effects on the properties of electron donor-acceptor (EDA) complexes has received little attention<sup>1-4</sup>. Our data compiled in Table 1 now show, that small but significant hypsochromic shifts of the CT-transition occur upon deuteration in the donor for various complexes between aromatic donors and strong pi-electron acceptors.

Table 1	Donor	Acceptor	Solvent (20°C)	$\lambda_{CT}$ (nm)	$\Delta h\nu_{CT}^a$ (cm <sup>-1</sup> )
	benzene	TCNE <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	388.2±0.2	0 ± 10
	benzene-d <sub>6</sub>	TCNE	CH <sub>2</sub> Cl <sub>2</sub>	388.2	
	toluene	TCNE	CH <sub>2</sub> Cl <sub>2</sub>	412.6	41
	toluene-d <sub>8</sub>	TCNE	CH <sub>2</sub> Cl <sub>2</sub>	411.9	
	p-xylene	TCNE	cyclohexane	405/465.5	141
	p-xylene-d <sub>10</sub>	TCNE	cyclohexane	405/462.5	
	HMB <sup>c</sup>	TCNE	CH <sub>2</sub> Cl <sub>2</sub>	539.6	72
	HMB-d <sub>18</sub>	TCNE	CH <sub>2</sub> Cl <sub>2</sub>	537.5	
	HMB	chloranil <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	518.8	86
	HMB-d <sub>18</sub>	chloranil	CH <sub>2</sub> Cl <sub>2</sub>	516.5	

<sup>a</sup> Shift of CT maximum upon deuteration. <sup>b</sup> TCNE = tetracyanoethylene. <sup>c</sup> HMB = hexamethylbenzene. <sup>d</sup> Chloranil = tetrachloro-p-benzoquinone.

The shift does not occur upon exclusive substitution of aromatic hydrogens but only upon substitution of benzylic hydrogens (cf. Fig. 1), which excludes an inductive mechanism. An explanation based upon steric effects would require a larger complex separation<sup>5</sup> for the deuterated donors but the steric requirements of -C-<sup>2</sup>H are actually known<sup>6,7</sup> to be less than those of -C-<sup>1</sup>H. Therefore the increase in CT transition energy is tentatively attributed to a slight increase of the donor ionization potential (I<sub>D</sub>) due to less effective hyperconjugative interaction of -C-<sup>2</sup>H than -C-<sup>1</sup>H with the donor pi-system<sup>8-10</sup>.

A unique confirmation of the hyperconjugative nature of the present effects comes from the behaviour of the p-xylene/TCNE complex. The two closely spaced CT-transitions shown by this system (cf. Fig. 2) can be attributed<sup>5</sup> to excitations involving the highest occupied level (HOMO) and the penultimate level (HOMO-1) of the donor respectively. Only HOMO can be influenced by conjugative substituent effects since HOMO-1 contains a nodal plane in which the substituent

tients lie (cf. Fig. 3).

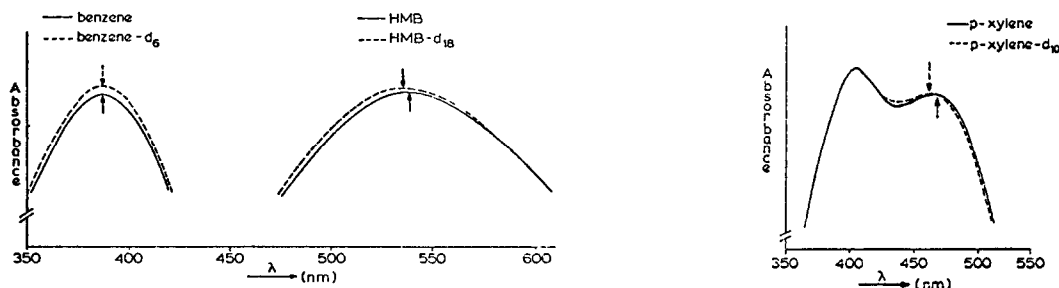


Fig. 1 CT absorption of benzene/TCNE and of HMB/TCNE. Fig. 2 CT absorption of *p*-xylene/TCNE.

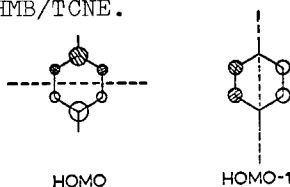


Fig. 3 Nodal properties of the two highest occupied MO's of *p*-xylene.

The effect of perdeuteration of *p*-xylene (cf. Table 1 and Fig. 2) thus corroborates our interpretation of the isotope effects since only a hypsochromic shift of the longest wavelength CT transition is observed while the second transition remains unaffected!

It seems important to note, that the changes in  $I_D$  due to benzylic deuteration as detected

by the present work are in principle sufficiently large (i.e. up to about 0.4 kcal/mol) to account for a significant kinetic isotope effect on one electron transfer reactions. This contrasts with the general (tacit) assumption, that in reactions involving one electron abstraction as a primary step—such as many oxidative side chain substitutions<sup>11-14</sup> of alkylaromatics—the electron transfer step is devoid of any isotope effect.

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