

INTRAMOLECULAR DONOR-ACCEPTOR INTERACTION IN

$\beta$ -ARYL-SUBSTITUTED CARBONIUM IONS

G.I.Borodkin, D.V.Korchagina, B.G.Derendjaev, and V.G.Shubin\*

Institute of Organic Chemistry, Siberian Division of the  
Academy of Sciences, 90, Novosibirsk, U.S.S.R.

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9-p-X-Phenyl-9,10-dimethylphenanthrenonium ions (Ia-e) have been shown to undergo a rapid twofold degenerate rearrangement by 1,2-p-X-phenyl shifts<sup>1</sup>. This rearrangement may be considered as electrophilic aromatic substitution reaction. Therefore, it is reasonable to expect some kind of donor-acceptor interaction between the aromatic ring to be attacked and the carbonium centre. The interactions of such a type were often postulated (for general discussion see ref.<sup>2</sup>; ref.<sup>3</sup> is also significant) and some intermolecular donor-acceptor complexes consisted of an electron donor and carbonium ion as acceptor (long-lived<sup>4</sup> or "to be born"<sup>5</sup>) were detected by spectral methods. However, as far as we know, there are no similar data on the intramolecular donor-acceptor complexes formed as a result of the interaction between an aromatic donor at C <sub>$\beta$</sub>  and carbonium centre (cf. <sup>6,7</sup>).

9-p-X-Phenyl-9,10-dimethylphenanthrenonium ions (Ia-e) appear to be rather good model compounds to detect such an interaction by a proper physical method. These ions are long-lived in contrast to the other  $\beta$ -aryl-substituted carbonium ions such as, e.g., 1,1,2-trimethyl-2-p-X-phenyl propyl cations, which undergo rapid isomerizations<sup>8,9</sup>. It is reasonable to expect that donor-acceptor interaction under consideration must show itself in the absorption spectra of the ions (Ia-e) as a charge-transfer band, frequency thereof being in a linear relationship with the ionization potential of the donor. Indeed

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\* To whom correspondence should be addressed.

we have found such bands in the absorption spectra of the ions (Table, Fig. 1). The intramolecular nature of the donor-acceptor interaction follows from the fact that observed charge-transfer absorption obeys Beer's Law (concentration range studied  $10^{-3}$ - $10^{-5}$  M). In contrast to these spectra the absorption spect-

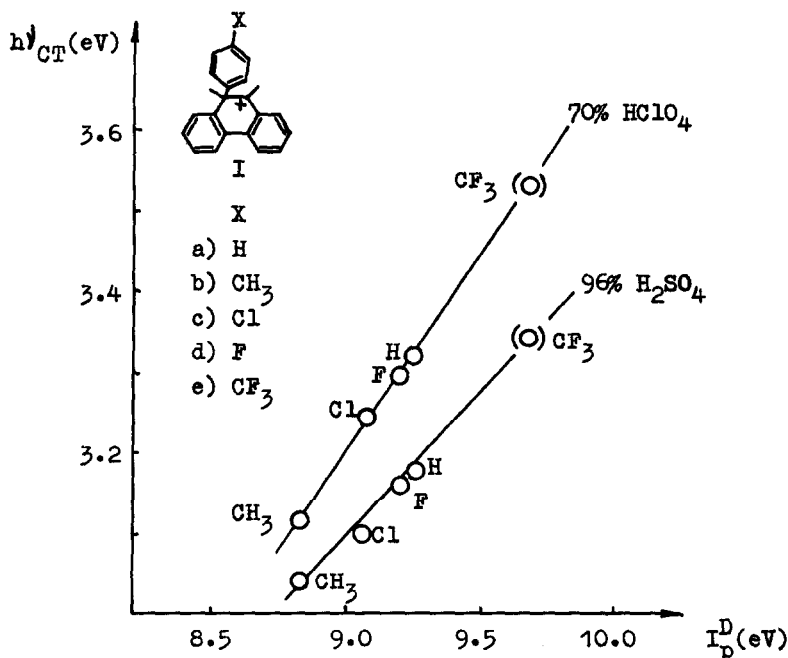


Fig. 1. ( $I_p^D$  are the ionization potentials of the p-X-substituted benzenes <sup>10</sup>)

rum of the closely related but having no  $\tilde{\pi}$ -electron donor at C<sub>9</sub>, 9,9,10-trimethylphenanthrenonium ion, shows no charge-transfer band.

In addition, the restricted rotation of the p-X-phenyl groups around the C<sub>9</sub>-C<sub>Ph</sub> bond in the ions (Ia-e) have been revealed by NMR. The most populated conformation is that outlined in Fig. 2 as it follows from detailed analysis of the NMR spectra of the ions (to be published separately), the estimated rotational barrier,  $\Delta G^\ddagger$ , for the ions (Ib,c,e) being  $8.5 \pm 0.1$  kcal/mole at  $-100^\circ\text{C}$  in  $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$  (1:10). It may arise from "pure" steric effects only, however, some contribution of the donor-acceptor interaction between p-X-phe-

Table

Absorption spectra of 9-p-X-phenyl-9,10-dimethylphenanthrenonium ions at 25°C

X	$\lambda_{\max}$ , nm (lg $\epsilon$ )					
	in 96 % H <sub>2</sub> SO <sub>4</sub>			in 70 % HClO <sub>4</sub>		
		CF <sub>3</sub> -band			CF <sub>3</sub> -band	
H	270(4.42)	390(3.52)	555(3.77)	269(4.50)	373(sh)	558(3.79)
CH <sub>3</sub>	271(4.54)	407(3.45)	561(3.72)	269(4.41)	397(3.50)	558(3.70)
Cl	270(4.46)	400(3.46)	559(3.74)	270(4.46)	382(3.54)	556(3.75)
F	269(4.49)	393(3.42)	556(3.74)	269(4.50)	376(sh)	556(3.81)
CF <sub>3</sub>	271(4.47)	333(3.94)	556(3.81)	269(4.49)	*	556(3.84)
9,9,10-tri- methylphenan- threnonium ion	266(4.28)	338(3.92)	530(3.59)**	267(4.29)	339(3.89)	538(3.64)

\*  $\lambda_{\max}$  is probably about 370 nm (for the solution in 96% H<sub>2</sub>SO<sub>4</sub>) and about 350 nm (for the solution in 70% HClO<sub>4</sub>), the band being overlapped with the neighbour short-wave one.

\*\* In 75% H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup>

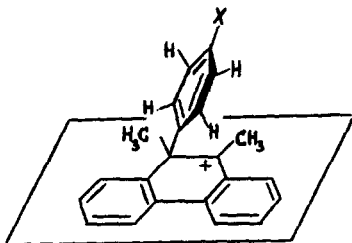


Fig. 2.

nyl group at C<sub>9</sub> and carbonium centre cannot be ruled out ( cf. ref.<sup>12</sup> ).

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