E2-31: Substituent effect on the intramolecular electron transfer of 9-anthracene methyl benzoate esters in methanol

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The photoinduced intramolecular electron transfer (PIET) between the 2 chromophores connected through σ-bonds has been studied thoroughly. Recently it was found that the lower fluorescence quantum yields in naphthylmethyl benzoate esters were due to the PIET between the naphthyl and the benzoate chromophores. The s-cis conformation of the ester is necessary for the PIET. In this study the preparation and fluorescence quantum yields of a series of substituted 9-anthracene methyl benzoate esters in methanol is reported. This data permits estimation of the PIET rates.

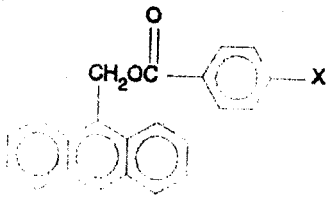
A series of substituted 9-anthracene methyl benzoate esters 1a-1e were prepared by mixing 9-anthracene methanol with the corresponding acid chloride in benzene in the presence of pyridine. These esters were purified by chromatography on silica gel and crystallized from CH_2Cl_2/hexane. The fluorescence quantum yields of these esters in methanol were measured, using 9-anthracene methyl acetate as the reference and corrected for the emission wavelength.

All the compounds were identified by NMR, GC/MS, and IR spectroscopy. The melting points were:
1a : 57°C, 1b : 129°C, 1c : 121°C, 1d : 132°C, 1e : 75°C.

The corrected quantum yields were measured in methanol
(*Table 1*). The florescence quantum yields of 1b and 1d are higher than that of 1a, whereas the fluorescence quantum yields of 1c and 1e are lower than that of 1a. This data suggests that the PIET from the anthracene chromophore to the benzoate chromophore is strongly dependent on the benzoate ring.

Table 1 : Corrected fluorescence quantum yield of la-e.

Compound	*Quantum Yield*
la	0.280
lb	0.292
lc	0.028
ld	0.287
le	0.270



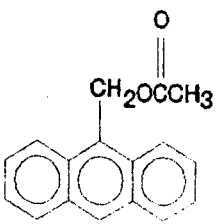
la:	X = H
lb:	X = 4-OCH_3
lc:	X = 4-NO_2
ld:	X = 4-CH_3
le:	X = 4-Br

la: X = H
lb: X = 4-OCH3
lc: X = 4-NO2
ld: X = 4-CH3
le: X = 4-Br

The electron donating groups in the benzoate ring reduce the reduction potentials of the benzoate ring and therefore, decrease the PIET rates causing increase in the fluorescence quantum yields. On the other hand electron accepting groups in the benzoate ring enhance the PIET rates reducing the fluorescence quantum yields. The Hammet plot for the PIET rates is a straight line as given in *Figure I.*

Table I: Corrected Fluorescence Quantum Yields of 1 and 2.

Compound	methanol	0.01M β- cyclodextin
1	0.300	0.300
2	0.028	0.072



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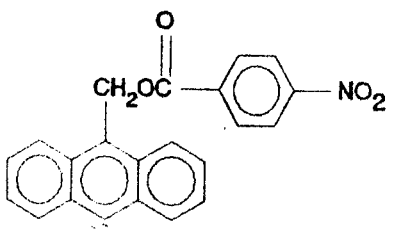

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