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FLUORESCENCE FROM INTER- AND INTRAMOLECULAR CHARGE-TRANSFER COMPLEXES

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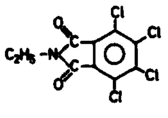
Introduction

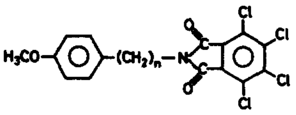
Intermolecular charge-transfer (CT) complexes, showing fluorescence in (liquid) solution, have only been reported[1] with tetrachlorophthalic anhydride, pyromellitic dianhydride or 1,2,4,5-tetracyanobenzene as an electron acceptor, and some (methyl substituted) aromatic hydrocarbons as electron donors.
Recently intramolecular CT fluorescence was reported[2] for p-$O_2NC_6H_4(CH_2)_nNHAr$ (n = 1, 2), but in this case a corresponding intermolecular complex is not fluorescent. We have found that CT fluorescence can be observed with inter- and intramolecular complexes containing the N-alkyltetrachlorophthalimide group as an electron acceptor and a variety of aromatic compounds as electron donors.

Results and discussion

In Table 1 the fluorescence maxima observed for some intermolecular CT complexes involving N-ethyltetrachlorophthalimide (I) as an electron acceptor are given. The complexes were excited in the long wavelength absorption maximum of the acceptor (29,700 cm^{-1}, ε = 2500). The acceptor alone is not fluorescent under the same conditions (CCl_4 solution at room temperature).
In most complexes CT absorption can be detected as a weak long wavelength absorption tail, and the excitation spectra show a long wavelength shoulder or tail corresponding with excitation in this CT absorption.



I



II

Table 1

CT fluorescence maxima in carbontetrachloride solution at 20°, from corrected emission spectra.

complex	fluorescence	
	$\tilde{\nu}_{max}$(cm^{-1}x10^3)	λ_{max}(nm)
I/mesitylene	23.3±0.2	429
I/durene	21.4	467
I/pentamethylbenzene	21.1	474
I/hexamethylbenzene	20.4	490
I/anisole	21.1	474
I/*p*-methylanisole	19.6	510
I/1,4-dimethoxybenzene	17.2	581
I/carbazole	19.0	526
II (n = 3)	19.3	518
II (n = 4)	19.9	503

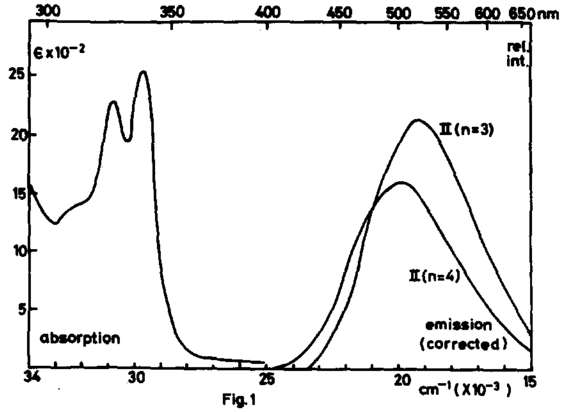


Fig.1

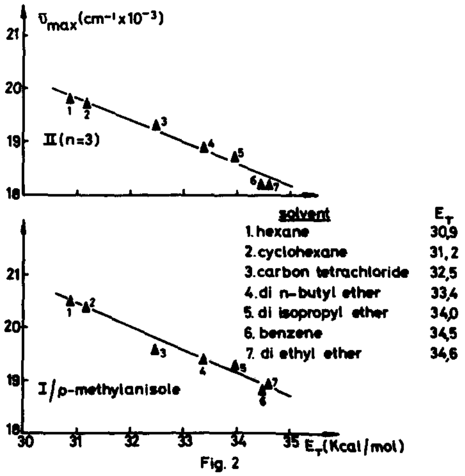


Fig. 2

Furthermore Fig. 1 and Table 1 show some spectral data obtained for compounds II.

Compounds II (n = 1-4) show weak absorption at long wavelength due to intramolecular CT interaction between both chromophores in the ground state[3,4]. Upon excitation in this CT absorption or in the absorption maximum at 29,700 cm^{-1} (which stems from the tetrachlorophthalimide chromophore) fluorescence is observed for II (n = 3) and II (n = 4). This fluorescence falls in the same frequency region (within 600 cm^{-1} cf. Table 1) as that observed for the comparable intermolecular complex between I and p-methylanisole.

For II (n = 1) and II (n = 2) fluorescence is extremely weak if existent at all. The CT character of the fluorescence maxima compiled in Table 1 is supported by the extreme solvent sensitivity of their positions, which are linearly correlated to the solvent E_T[5] values as shown in Fig. 2 for II (n = 3) and for the complex between I and p-methylanisole. Since E_T values do refer to the position (in kcal/mole) of an electronic absorption for a molecule with a dipolar ground state, the linear correlation found in Fig. 2 indicates that the fluorescence observed occurs from an essentially zwitter-ionic excited state, in accordance with a one electron transfer.

In strongly polar solvents the CT fluorescence is quenched, probably because of facile dissociation of the highly polar excited complex[6,7].

It has recently been pointed out[1] that the equilibrium geometry of CT complexes in the excited state may differ appreciably from that in the ground state. Thus for CT complexes in solution, reorientation to the excited state equilibrium geometry takes place after excitation and prior to fluorescence.

For compounds II the methylene chain between the two chromophores limits their possible orientations. It is therefore interesting to note that compounds II (n = 1,2), which do show (weak) intramolecular CT absorption[3,4], are not fluorescent, while the more flexible compounds II (n = 3,4) show CT fluorescence although their CT absorption is not significantly stronger.

Rapid reorientation in the excited state, leading to the formation of intramolecular excimers or exciplexes, has been observed for compounds $Ar-(CH_2)_3-Ar'$[8,9].

Further research to reveal the conformational requirements for CT fluorescence in compounds like II, also with other chromophores, is in progress.

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