

STUDIES OF INTER- AND INTRA-MOLECULAR DONOR-ACCEPTOR INTERACTIONS—IX INTRAMOLECULAR CHARGE TRANSFER INTERACTION IN ARALKYL 2,4,6-TRINITROBENZOATES

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Abstract—UV spectra were studied of compounds containing an aryl group as an electron donor and the 2,4,6-trinitrobenzoate group as an electron acceptor linked by a chain of one to three methylene groups. The following aryl groups were investigated:

p-anisyl, 2,5-dimethoxy and 2,4,6-trimethoxyphenyl, 1- and 2-naphthyl, 9-anthryl and 1-pyrenyl.

Only the compound with a 1-pyrenyl group linked to the 2,4,6-trinitrobenzoate group by a trimethylene chain shows a *discrete intramolecular C(harge) T(ransfer) transition*.

The molecule adopts a folded conformation as confirmed by its NMR spectrum.

INTRODUCTION

WE HAVE shown¹ that *intramolecular C(harge) T(ransfer) interaction* can occur in systems



in which D is a neutral aromatic electron donor and A is a *positively charged* (e.g. a substituted pyridinium ion) or a *neutral* electron acceptor (e.g. a substituted aromatic imide). In a study of intermolecular CT complexes it was found that methyl 2,4,6-trinitrobenzoate has good acceptor properties which are fully comparable with those of 1,3,5-trinitrobenzene.² The present paper describes a study on the occurrence of *intramolecular CT interaction* in systems containing an aryl group as an electron donor and the 2,4,6-trinitrobenzoate group as an electron acceptor.

RESULTS

For the compounds, compiled in Table 1, the possible interaction between the electron donor (e.g. the aryl group) and the electron acceptor (e.g. the 2,4,6-trinitrobenzoate group) was studied both by UV and NMR spectroscopy.

Intermolecular complex formation between aromatic electron donors and methyl 2,4,6-trinitrobenzoate (TNMB) leads to characteristic longwave UV absorptions and to strong upfield shifts of the aromatic protons of TNMB in NMR.²

For instance concentrated chloroform solutions of pyrene, anthracene and TNMB give rise to discrete intermolecular CT transitions (c.f. Fig 1) with $\lambda_{\max} = 465 \pm 1$ and 475 ± 1 nm resp. In Figs 2 and 3 the absorption spectra of XVIII, XIX, XX, XXII and XXIII containing the same combination of donor and acceptor are shown in a concentration at which intermolecular CT interaction cannot be detected.

TABLE I. CHEMICAL SHIFT OF THE 2,4,6-TRINITROBENZOATE PROTONS IN CHCl_3 AT 25° (0.01 M) RELATIVE TO TMS

Code	R	n	Chemical shift (Hz at 100 MHz)
I	Methyl	0	930.7 ± 0.1
II	phenyl	1	928.6
III		2	927.6
IV		3	930.0
V	<i>p</i> -anisyl	1	928.2
VI		2	928.1
VII		3	929.3
VIII		4	928.9
IX	2,5-dimethoxyphenyl	1	924.9
X		2	926.5
XI		3	929.2
XII	2,4,5-trimethoxyphenyl	2	927.5
XIII		3	930.5
XIV	1-naphthyl	1	927.3
XV		2	927.4
XVI	2-naphthyl	1	929.8
XVII		2	925.4
XVIII	9-anthryl	1	922.6
XIX		2	926.7
XX		3	928.5
XXI	1-pyrenyl	1 ^a	—
XXII		2	929 ^b
XXIII		3	867.6

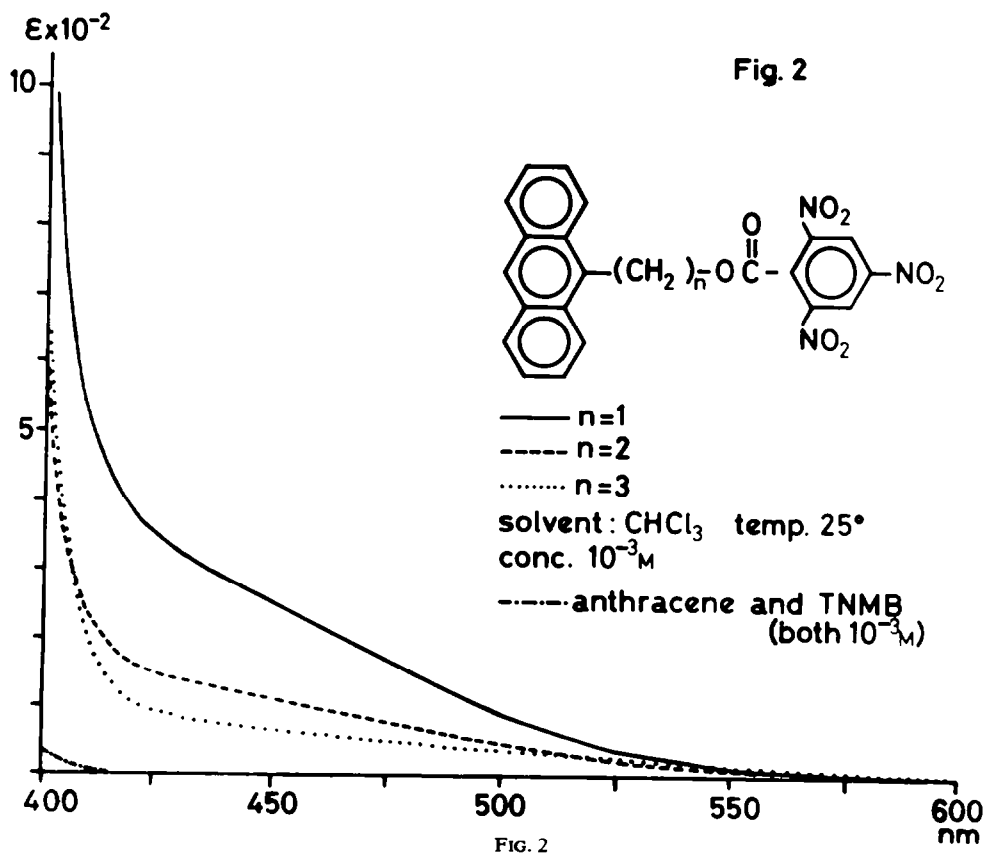
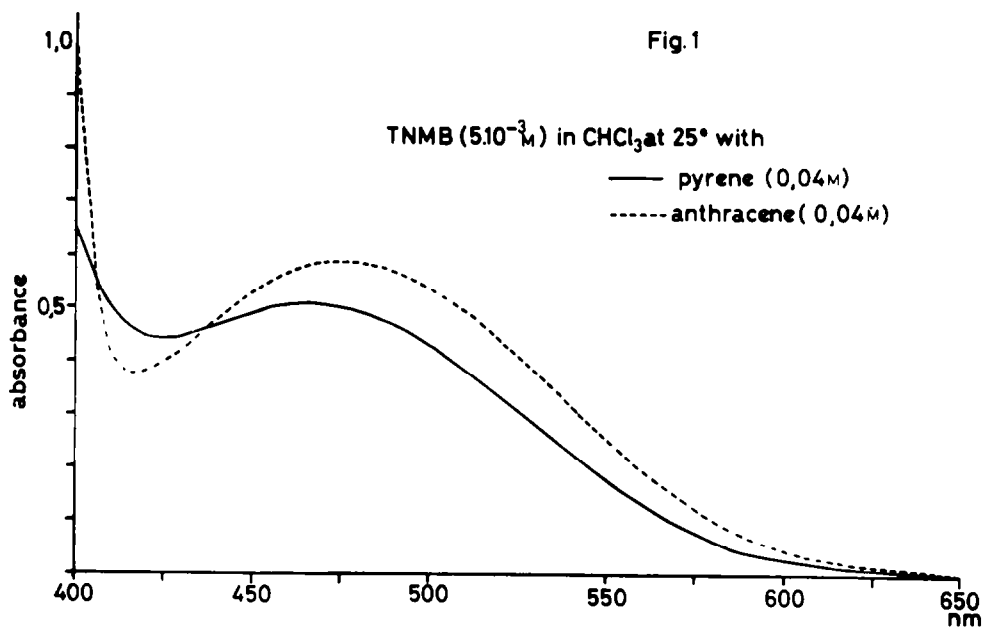
^a Not obtainable in pure form because of instability

^b Due to its low solubility this compound was measured at ca. 0.001 M by time averaging over 500 scans

Practically all compounds from Table 1 show weak longwave absorption tails, which were found to obey Beer's law. Only XXIII (*cf* Fig 3) shows a discrete long-wave absorption maximum ($\lambda_{\text{max}} = 475 \pm 1$ nm and $\epsilon_{\text{max}} = 194$). Furthermore the chemical shift of the aromatic protons of the trinitrobenzoate group was measured for the compounds in Table 1 at a concentration of 0.01 M at 25° (*cf* Table 1). In this concentration range shifts due to intermolecular interaction are small (0.8 Hz at 100 MHz). Only compound XXIII revealed a significant upfield shift for the aromatic protons in comparison with TNMB (63.1 Hz).

DISCUSSION

These results clearly indicated that, with one exception, *intramolecular* CT inter-



action between D and A in the cases studied does not lead to the observation of discrete absorptionmaxima. This may have three prominent reasons:

(i) Tendency for complex formation between D and A is too low to make a large fraction of the molecules adopting a conformation suitable for CT interaction and (ii) The maximum of the intramolecular CT transition is at too short a wavelength to make it discretely observable. This may occur if the ionization potential of the donor is relatively high² and (iii) The conformations suitable for CT interaction are made unfavourable by steric factors.

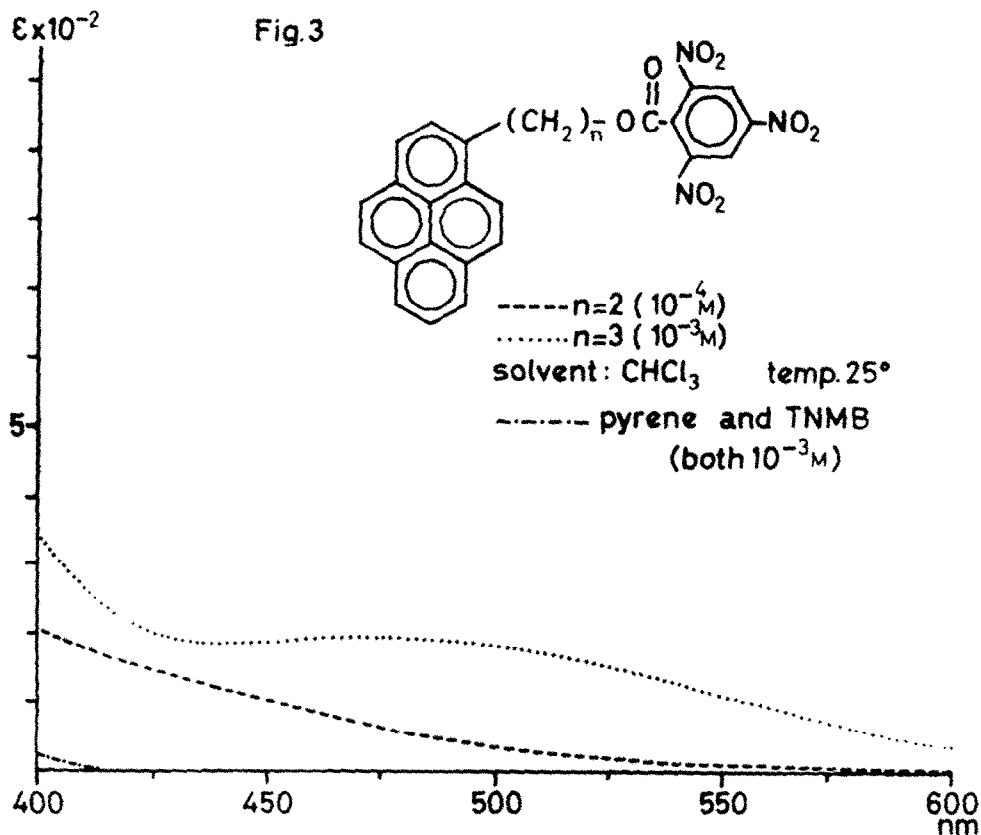


FIG. 3

Previous studies have shown² that especially anthracene and pyrene form stable intermolecular complexes with TNMB ($k = 2.9 \pm 0.3$ and 3.4 ± 0.2 l/mole at 25° resp.) showing discrete intermolecular CT transitions (cf Fig 1).

Obviously the compound XXIII in which the donor (e.g. pyrene) and the acceptor are separated by a trimethylene chain can exist in a conformation suitable for CT interaction. The factors (i) and (ii) seem sufficient to explain the absence of any significant chemical shift for the protons of the trinitrobenzoate group in the NMR spectra and of a discrete intramolecular CT transition in the UV spectra of all

compounds from Table 1, except for those containing anthracene and pyrene as a donor part.

It is generally accepted^{3,4} that the intensity of CT transitions is mainly governed by the extent of overlap between the donor- and acceptor-electron clouds.

For compounds D-(CH₂)_n-A with *n* = 1 only a limited degree of overlap ("homo-conjugation") is possible, which nevertheless may lead to the observation of intramolecular CT transitions⁵ as is also shown by the longwave absorption of XVIII.

For compounds with *n* = 2 conformations in which the electron clouds of D and A overlap are sterically very unfavourable as indicated by model studies.

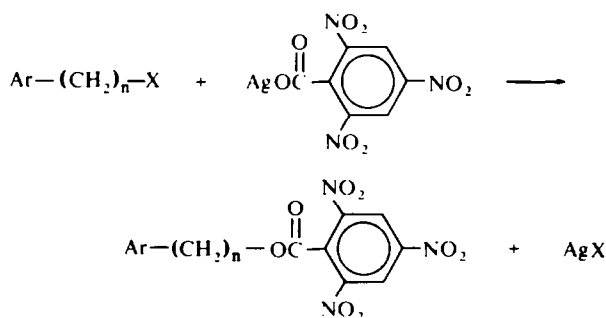
For these systems factor (iii) therefore seems dominant. In contrast however Dewar c.s.⁶ observed rather large upfield shifts for the toluene protons of 2-(1-pyrenyl)-ethyl-*p*-toluene sulphonate indicating, in this case, proximity of the pyrene and the *p*-toluenesulphonate groups.

Steric factors probably exclude such a proximity when a *p*-toluenesulphonate group is replaced by a trinitrobenzoate group. Studies on excimer fluorescence,⁷ hypochromicity⁸ and intramolecular radical dimerization⁹ have shown that compounds with *n* = 3 can easily adopt a folded conformation, which leads to close contact between D and A. This conformation may be responsible for the occurrence of the observed intramolecular CT transition in XXIII.

In spite of the comparable stabilities and absorption maxima of the *intermolecular* complexes of TNMB with anthracene and pyrene no discrete *intramolecular* CT transition and no chemical shift of the aromatic protons of the 2,4,6-trinitrobenzoate group is observed for XX. In our opinion this must be attributed to some steric destabilization of the folded conformation in the latter case. This problem will be discussed more explicitly in a subsequent paper.¹⁰

EXPERIMENTAL

The following reaction scheme¹¹ was used for the preparation of the aralkyl 2,4,6-trinitrobenzoates:



in which X = Cl or Br for *n* = 1
and X = I for *n* > 1

The reaction was carried out by refluxing the two reactants in dry benzene for 6–15 hr. Details of the syntheses will be given elsewhere.¹²

UV spectra were recorded on a Cary Model 14 recording spectrophotometer at 25° in spectrograde chloroform (Merck-UVASOL) in cells with 1 and 10...cm pathlength. NMR spectra were recorded on a Varian HA100 spectrometer at 25° in deuterated chloroform with TMS as an internal reference.

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