

LASER FLASH PHOTOLYSIS STUDIES ON THE TRIPLET STATE OF AROMATIC HYDROCARBONS IN THE VAPOUR PHASE*

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Summary

Triplet-triplet ($T_1 \rightarrow T_n$) absorption spectra under low resolution and decay times have been measured for a variety of simple fluorine-substituted benzenes in the vapour phase. Assignments for the observed transitions were made on the basis of CNDO calculations and comparison with the corresponding ${}^3B_{1u} \rightarrow {}^3E_{2g}$ transition in benzene. Decay times measured were in the region 200 - 250 ns, orders of magnitude shorter than the corresponding decay time for benzene itself. Reasons for this shortening are briefly discussed.

1. Introduction

Direct dynamic studies on the triplet states of benzenoid hydrocarbons in the vapour phase are carried out only with experimental difficulty owing to the fact that the states are non-phosphorescent, the triplet-triplet (T-T) absorption occurs in a relatively inaccessible region of the spectrum (200 - 250 nm) [1] which is also overlapped by ground state absorptions ($S_0 \rightarrow S_2$) and indirect measurements indicate lifetimes to be in the submicrosecond region rendering conventional flash photolysis methods impossible [2]. Such measurements are of interest, however, in that the effects of substitution [3] appear to be dramatic, particularly in the case of fluorobenzenes in which there is a large decrease in triplet decay time upon substitution with even a single fluorine atom [3]. Methyl substitution has a less dramatic effect [1].

The results reported here represent attempts to obtain quantitative data on a variety of simple substituted benzenoid hydrocarbons in the vapour phase using laser flash photolysis methods.

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2. Experimental

The lifetimes were determined by measuring the decay in the transient absorption of the benzenes under study which were excited by a pulse of frequency-quadrupled light from a neodymium laser and monitoring the absorption using light from a 75 W xenon arc lamp passing at right angles to the laser pulse. The xenon arc was driven by a power supply (15 V, 5 A, DCA) including a pulsing unit (90 V, 1 ms) made in the laboratory. After passing through the cell, the monitoring light beam entered a Jobin-Yvon monochromator (type Georgie). An RTC 53 UVP photomultiplier tube of S13 response powered by a Saphymo HTT 2503 power supply measured the light intensity output from the monochromator and the signal was led to either a Schlumberger O.C.M. 581 C storage oscilloscope or a Tektronix type 585 A oscilloscope. On both oscilloscopes, differential plug-ins including an offset voltage source were used since the transient optical densities were less than 0.1. The oscilloscope was triggered by a diode placed after the second amplifier of the laser. An Oscillophot M5 Polaroid camera manufactured by Steinheil Optronic was fitted to the oscilloscope and used to photograph the traces using a type 47 Polaroid high speed film.

The laser beam was amplified by the two amplifier heads and then frequency doubled twice by two potassium dihydrogen phosphate (KDP) crystals maintained thermostatically at 26 °C. The beam was then focused onto a silica cell of 1 cm square cross section containing the gaseous sample using a cylindrical lens of focal length 8 cm placed about 6 cm in front of the cell such that the excitation area was a square of 0.3 cm². The power of each laser pulse was monitored by a diode head placed between the oscillator and the first amplifier head. After each pulse a photograph was taken of the resulting transient trace and an enlargement made from which optical densities could be measured as a function of time.

The analysing lamp was triggered as follows to determine the transient absorptions. The signal triggering the firing of the laser flash lamps was applied to the pulsing unit of the xenon arc power supply through a delay arranged in such a way that the analysing light pulse reached its maximum intensity just before the laser pulse. This system allows the top almost flat part of the analysing light pulse to be used to view the transient absorption, thus providing much more intensity for the far UV region being studied.

The optimum characteristics of the laser pulse are defined as 30 J, at 1.06 μm , in 30 ns with up to 1 GW power and a divergence of less than 3×10^{-4} rad. However, in these experiments the actual pulse obtained tended to be about 50 ns at half height and could be up to 70 ns at the base, the energy at 264.5 nm after the two frequency doublings and filtrations being around 50 mJ per pulse. Nevertheless, the pulse characteristics were satisfactory for the purpose of these experiments.

A block diagram of the laser system used in these experiments is given in Fig. 1.

The original laser system utilizing parallel excitation and analysing beams gave poor results with many optical artefacts. This was possibly due

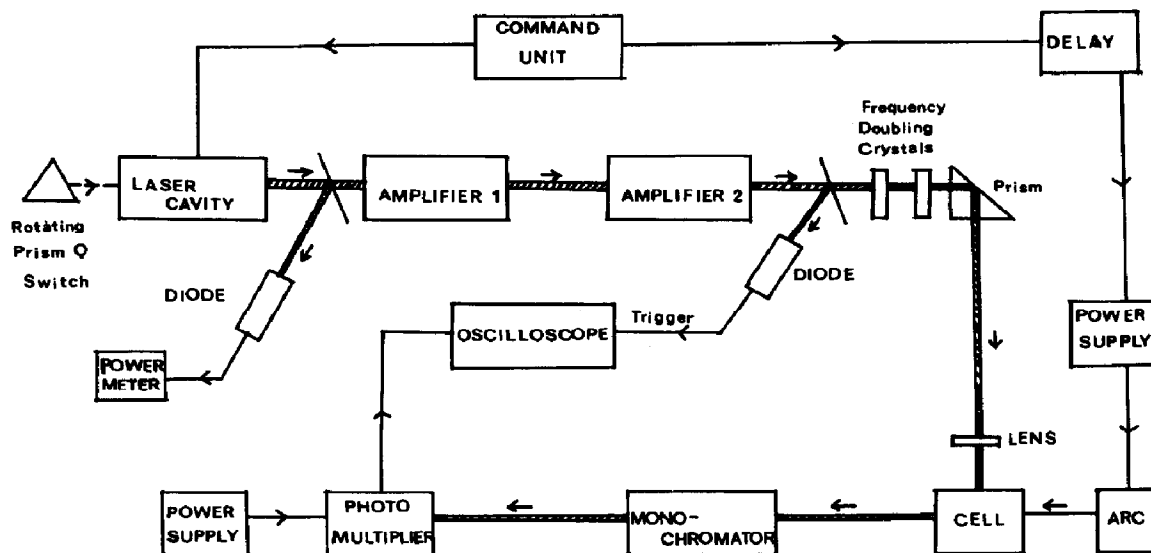


Fig. 1. Schematic diagram of the laser flash system.

to only partial absorption taking place within the analysing beam leading to apparent secondary products indicated by a rise in the base line of the oscilloscope after the decay of the triplet transient and existing on a much longer time scale of the order of a microsecond. Various postulates of two-photon processes [4], formation of radicals [5] or large permanent product formation were all eliminated as the systems, both optical and electronic, were improved and tuned, and the artefacts were removed.

2.1. Materials

The materials used were as follows:

<i>para</i> -difluorobenzene	} Fluorochem pure and Puriss grade approximately 99.6% pure
<i>meta</i> -difluorobenzene	
<i>ortho</i> -difluorobenzene	
1,4-bis(trifluoromethyl)benzene	
<i>para</i> -fluorotoluene	} Koch Light pure grade
<i>meta</i> -fluorotoluene	

Purities were checked by gas-liquid chromatography and all materials distilled in the middle third were retained for use.

3. Results and discussion

The series of compounds studied here were *ortho*, *para* and *meta* difluorobenzene, *para* and *meta* fluorotoluene and *para* and *meta* hexafluoroxylene. All of these, apart from the last, are well suited for study by the frequency-quadrupled light from the neodymium laser (264.5 nm) as this wavelength almost coincides with the $(0,0 + \nu_1)$ singlet absorption band of

all of the fluorobenzenes. In the case of the hexafluoro-*meta*-xylene 264.5 nm corresponds to a well between the two peaks in the absorption spectrum and, owing to the low extinction coefficient, no transient is seen.

3.1. Transient absorptions

The results obtained are presented in Table 1 along with those obtained by Stevens *et al.* [3] for fluorobenzene and pentafluorobenzene. In all cases the transient absorption to the blue of the S_0-S_1 transition was found to be greatest at about 230 nm (Fig. 2) but measured optical densities were very low, in the region of 0.08 - 0.1. This leads to estimated extinction coefficients for the T-T absorption of the order of 10^{-3} , but large error limits are imposed primarily by the presence of a relatively long lived absorption in all cases which makes a precise determination of the optical density of the transient difficult. A further difficulty was due to the variation of the exciting light intensity from pulse to pulse by a factor of up to 20% so that normalization of the pulse power was necessary in each case for comparison of the results.

In all cases the lifetime of the transient was markedly reduced by the addition of about 100 Torr of oxygen to the sample. When an atmosphere of air was allowed to enter the cell, the absorption due to the transient was completely quenched out. Since excited singlet states of these compounds have also been shown to be susceptible to quenching by oxygen, this cannot be taken as unequivocal evidence that the transient is the triplet state in each case. However, the excited singlet state is certainly much shorter lived than the transients measured here [6], and it also seems reasonable to suppose that the principal processes through which the singlet state is quenched are

TABLE 1
Triplet lifetimes

Compound	Singlet-singlet absorption band excited (nm)	Pressure (Torr)	Triplet lifetime
Benzene ^a	264.4	20	26 μ s
Monofluorobenzene ^b	265.4	3.7	250 \pm 80 ns
<i>para</i> -difluorobenzene	259.32	10	200 \pm 20 ns
<i>ortho</i> -difluorobenzene	259.02	20	260 \pm 40 ns
<i>meta</i> -difluorobenzene	259.03	15	340 \pm 40 ns
Pentafluorobenzene ^b	259.3	3.7	140 \pm 50 ns
Parafluorotoluene	265.4	15	290 \pm 20 ns
<i>meta</i> -fluorotoluene	262.4	20	400 \pm 40 ns
Hexafluoro- <i>para</i> -xylene	265.5	15	560 \pm 50 ns
Hexafluoro- <i>meta</i> -xylene		15	> 2 μ s ^c

^aIndirect measurement by Parmenter and Ring [13].

^bFrom ref. 3.

^cEstimated value.

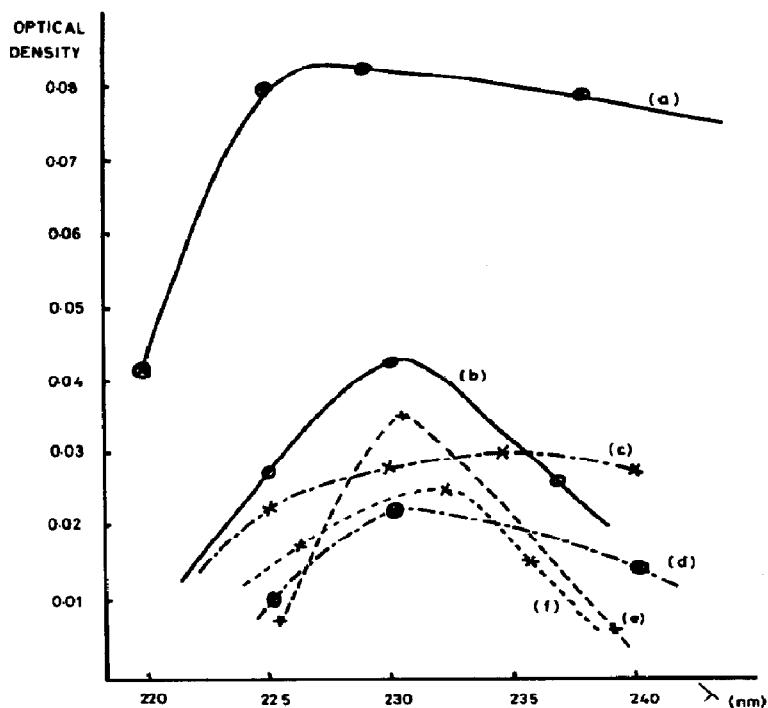
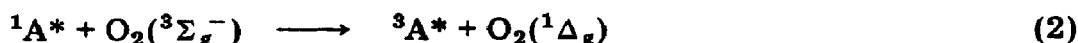
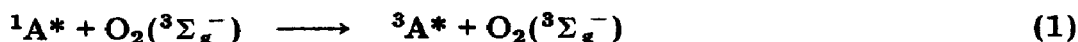


Fig. 2. T-T absorption spectra of substituted benzenes in the vapour phase at 25 °C: (a) *p*-difluorobenzene; (b) *m*-difluorobenzene; (c) *o*-difluorobenzene; (d) *m*-fluorotoluene; (e) *p*-fluorotoluene; (f) hexafluoro-*p*-xylene.



which actually populate the triplet level [7]. The observed quenching of the transient by addition of oxygen thus points to its being the triplet state.

Further support for this comes from consideration of the spectral position of the absorption of the transient species in each case. In the case of benzene, the absorption at 230 nm has been identified as that due to the ${}^3B_{1u} \rightarrow {}^3E_{2g}^-$ transition [8].

CNDO calculations, using both the S_1 and S_2 modifications [9, 10], have been carried out on benzene and some of its simply substituted derivatives. The program was developed to predict the energies and symmetries of the lowest 30 singlet and triplet states that are accessible from the singlet ground state. Application of conventional selection rules for optically allowed transitions enables identification of the states which will give rise to an absorption from the lowest triplet state in the region studied, *i.e.* 220 - 250 nm. The results of these calculations for benzene and two of its fluorinated derivatives are presented in Table 2, where T_n is the energy of the state to which absorption occurs. These states are derived from the E_{2g}^- state of benzene and their symmetries are given in parentheses. A reduction in sym-

TABLE 2
CNDO calculations on triplet states

Compound	Program	Calculated energy levels ^a		ΔE (cm ⁻¹)	
		T ₁ (cm ⁻¹)	T _n (cm ⁻¹)	Calculated Transient maximum	
Benzene	CNDO/S1	(³ B _{1u}) 29 843	(³ E _{2g} ⁻) 76 301	46 458	43 554
Fluorobenzene	CNDO/S2	(³ A ₁) 24 197	(³ B ₁) 68 074	43 877	43 554
Hexafluoro- <i>para</i> -xylene	CNDO/S2	(³ B _{2u}) 30 650	(³ B _{2g}) 72 268	41 619	
			(³ B _{1g}) 73 494	42 830	42 910
			(³ A) 73 560	43 635	

^aStates given in parentheses.

metry is caused by substitution of the two CF₃ groups and leads to a splitting of the degenerate ³E_{2g}⁻ state. Although absorption is allowed to both of these levels, the T-T absorption spectrum could not be resolved using the present experimental system. It can be seen from Table 2 that the observed transients can be reasonably assigned to T-T absorption. Full details of the calculations will be given later.

3.2. Decay times

The decay times reported in Table 1 are incomplete as far as full discussion is concerned since there is evidence that in benzene the triplet state is self-quenched [11] by the ground state:



A full pressure study is required in order to be able to extract the self-quenching rate constant k_Q and the first order rate constant k_{NR} for non-radiative decay of the triplet state. Unfortunately in the present study transients were observed only with the pressures shown in Table 1. Above and below these pressures absorptions were too weak to be observable. Complete data on these molecules must therefore await experiments using other more sensitive equipment.

The lifetimes obtained here, however, show several general trends.

(1) Increasing the number of fluorine substituent atoms on the benzene ring decreases the lifetime in the order benzene > fluorobenzene > *para*-difluorobenzene > pentafluorobenzene.

(2) Within one molecule, the position of the substituents affects the triplet lifetime in the order *para* < *ortho* < *meta* in both the difluorobenzene and fluorotoluene series.

(3) Insertion of substituents of different types decreases the triplet lifetime in the order *para*-difluorobenzene < *para*-fluorotoluene < hexafluoro-*para*-xylene.

It is evident that the presence of a fluorine atom and more particularly a CF_3 group greatly influences the non-radiative decay rate k_{NR} (eqn. (3)) in the molecules, since it is unlikely that k_{Q} will vary significantly. Since the $\text{T}_1 \rightarrow \text{S}_0$ non-radiative decay is a transition between purely $\pi\pi^*$ states, it is of necessity a transition of spin-orbit-vibronic coupling type involving a vibrational promoting mode.

Henry and Siebrand [12] have developed a theory of intersystem crossing processes in aromatic molecules in which both the spin-orbit coupling and the nuclear kinetic energy operators are treated as perturbations causing the non-radiative decay. The resulting general expressions for the matrix elements were shown to lead to three different mechanisms. The first, involving pure spin-orbit coupling, is subject to restrictive selection rules while the second and third involve spin-orbit-vibronic coupling. Studies on deuterium substitution in naphthalene and phenanthrene showed that the third mechanism involving one-centre integrals was dominant. Substitution at the carbon atoms with the highest electron density caused the greatest change to k_{NR} through its dependence on the spin-orbit and vibronic matrix elements. In the present case substitution by the highly electronegative F and CF_3 groups greatly changes the π electron density distribution; thus it is not surprising that large changes in k_{NR} result.

We are currently attempting a quantitative correlation of these effects with calculated rates.

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