

PHOTOCHEMISTRY OF TRIFLUOROMETHYL BENZENES IV. 1-FLUORO-2-(TRIFLUOROMETHYL)- AND 1-FLUORO-3-(TRIFLUOROMETHYL)-BENZENES

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SUMMARY

Quantum yields of fluorescence and intersystem crossing for the vapour of 1-fluoro-2-(trifluoromethyl)- and 1-fluoro-3-(trifluoromethyl)-benzene excited at various wavelengths corresponding to absorption in the first singlet band have been measured. Absolute rate constants for radiative and non-radiative decay of these compounds based upon these measurements and fluorescence decay times were derived, and data were compared with other substituted benzenes. Rate parameters for vibrational relaxation and quenching of the excited singlet and triplet states of the aromatic molecules were also measured.

INTRODUCTION

The perturbing effects of substituent groups upon the basic photophysics of benzene in the vapour phase has been investigated during the past few years. Thus the photochemistry of toluene^{1,2}, and the xylenes^{3,4} has been reported, and more recently, rate constants for radiative and non-radiative decay of all of the methyl-substituted benzenes in the vapour phase⁵ and in solution⁶ have been measured. A good correlation between magnitude of radiative rate constant and perturbation of molecular orbital symmetry was found, whereas the value of the non-radiative rate constant was shown to be independent of substitution. A similar correlation between radiative rate constant and position of substituent has been found for those members of the fluorobenzenes for which both decay times and quantum yield data are available^{5,7}. In addition, quantum yield measurements have been carried out on other members of the series⁸⁻¹².

Three of the trifluoromethyl benzenes have been investigated to date¹³⁻¹⁵, and fluorescence lifetime measurements again indicate a correlation of the type

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noted for other substituent groups¹⁶. It has been shown in the above studies that fluorine has by far the greatest perturbing effect upon the benzene system, and in molecules containing both fluorine and methyl groups, the fluorine was shown to play the dominant role. It seemed of interest therefore to study trifluoromethyl benzenes which also contained a fluorine substituent to compare the effects, and this work is reported here.

The quenching of excited singlet states of fluorine and methyl-substituted benzenes, and those containing both groups, by electronic energy acceptors such as ketones has been shown to occur with very large cross-sections¹⁷. A correlation has been noted between energy transfer efficiency and radiative lifetime of the excited state donor, as would be expected on the basis of a contribution to the total efficiency from Förster long-range dipole-dipole induced energy transfer¹⁷. Since the lifetimes of the molecules studied in this work have been measured, it seemed worthwhile to measure quenching efficiencies also.

EXPERIMENTAL

The apparatus used for these measurements was similar to that described in earlier reports^{10,12,13}, consisting of a conventional high vacuum system and fluorescence cell, and an optical system with associated electronics. The vacuum system was evacuated to a pressure of better than 10^{-5} Torr using a combination of rotary and two stage mercury diffusion pumps. Rotaflo Teflon barrel stopcocks or Springham greaseless stopcocks were used throughout. The fluorescence cell was 6 cm long \times 3 cm diameter and had a centrally placed 2 cm diameter emission window. The use of this cell has been described in an earlier report¹⁸.

Two light sources were used in this study, a Hanovia SH-100 medium pressure mercury lamp and an Osram XBO 150 xenon arc lamp, operated from a d.c. stabilized power supply. Exciting wavelengths were selected using a Bausch and Lomb 0.25 m focal length grating monochromator, with a grating blazed at 300 nm and with a reciprocal linear dispersion of 3.2 nm/mm. Transmitted light was measured by an RCA 935 phototube, and emitted light was detected by an RCA 1P28 photomultiplier tube. A 90 V dry cell and a Farnell EHT 2 power supply were used for the phototube and photomultiplier tube respectively. A Com-ing CS-7-54 filter was interposed between the fluorescence cell and photomultiplier tube for fluorescence measurements, and this was replaced by a CS-3-73 filter for measurements of the intensity of phosphorescence from biacetyl. Emission measurements were calibrated by use of benzene, for which the value of the fluorescence quantum yield at 20 Torr pressure, 253.7 nm excitation was taken as 0.18¹⁹, and for which the maximum quantum yield of sensitized phosphorescence of biacetyl under these conditions was taken as 0.105²⁰. Spectral response of the photodetectors was taken into account in the calibrations.

Pressures were measured on a mercury manometer, using expansion and

assumption of perfect gas laws for pressures below 2 Torr. Mixing was achieved by flash vaporization and standing for up to 12 hours. It was shown that such a procedure did not lead to quenching by leakage of air since the intensity of the long-lived triplet state emission from biacetyl was unaffected by overnight storage in the fluorescence cell.

RESULTS AND DISCUSSION

Spectra

The absorption spectra of 2 Torr 1-fluoro-2-(trifluoromethyl)- and 1-fluoro-3-(trifluoromethyl)-benzene in the region of the first absorption band taken on a Pye Unicam SP700 spectrometer at 23°C using a cell of 6 cm path length are shown in Fig. 1, together with the positions of the exciting wavelengths used in this study. High resolution fluorescence spectra are not available, but those obtained at 2 Torr pressure using a Farrand Mk. 1 spectrofluorimeter are shown in Fig. 2 normalized to the absorption spectra. It can be seen that despite lack of resolution, the profile of the fluorescence spectrum in each case bears a reasonable mirror symmetry relationship to the absorption spectrum. It was found that the spectral distribution of the fluorescence in each case was independent of pressure in the system. For

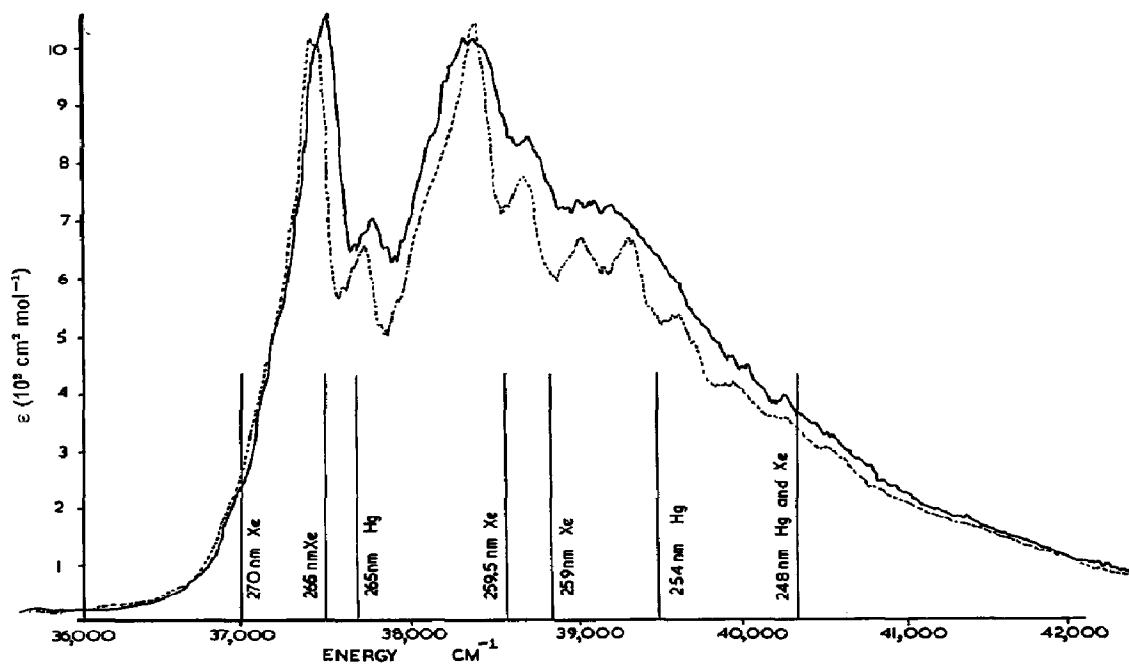


Fig. 1. Absorption spectra of 1-fluoro-2-(trifluoromethyl) (—) and 1-fluoro-3-(trifluoromethyl) (----) benzenes respectively. Vapour phase spectra taken on SP700 spectrophotometer with 6 cm cell, aromatic pressure 2.0 Torr. Positions of exciting wavelengths used in this study, and type of source are also indicated. Xe = Osram XBO 150 xenon lamp, Hg = Hanovia SH-100 medium pressure mercury lamp.

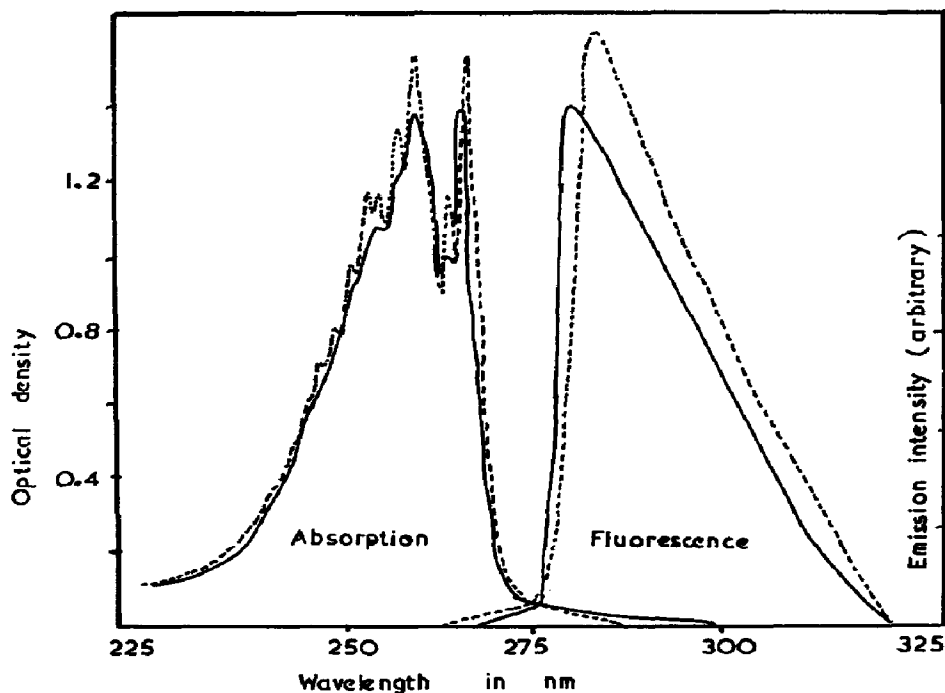


Fig. 2. Absorption and emission spectra of the two aromatic isomers. Emission spectra taken at 2 Torr pressure on Farrand Mk. 1 spectrofluorimeter and normalized to the absorption spectra.

well-resolved spectra, such as in benzene, change of shape of emission spectra with pressure is to be expected^{21,22}, but for molecules such as toluene studies under high resolution have shown that the spectral distribution does not change with excitation wavelength or pressure¹, owing to very fast unimolecular (and collisional) vibrational relaxation and redistribution prior to emission. Thus even for excitation in the collision-free zone, the emission is characteristic of a dense manifold of vibrational levels, and no significant change in the spectral envelope is to be expected with further collisional vibrational effects. It is not therefore surprising that the low-resolution fluorescence spectra in the present case are similarly pressure independent.

Figure 2 shows that there is little overlap between the absorption and emission spectra. In benzene, the transition from $^1A_{1g}$ ground state to $^1B_{2u}$ excited state is orbitally forbidden, the zero-zero transition is thus absent, and the maximum extinction coefficient has a value of ~ 200 . In the present case, the maximum value of the extinction coefficient is $\sim 10^3$, reflecting the perturbing effects of the substituents.

Under these circumstances, the zero-zero transition might be expected to be observable and from the spectral overlap in Fig. 2, the zero-zero transitions for the 1,2- and 1,3-isomers have been tentatively assigned at 272 and 270.5 nm respectively.

Use of these values together with the integrated molar absorptivities given by Ballester *et al.*²³ of 3.71×10^6 and 4.03×10^6 in the Forster equation²⁴ gives an estimated value for the mean radiative lifetimes $[(\tau_R)_{\text{calc.}}]$ for the 1,2- and 1,3-isomers of 70 and 64 nsec, respectively. It has been shown recently, however, that for fluorine (and probably trifluoromethyl) substituted benzenes, values of $(\tau_R)_{\text{calc.}}$ obtained by this method of integration of areas under absorption curves do not compare favourably with actual values obtained by fluorescence decay times and fluorescence quantum yields. This will be discussed further in a later section.

Quantum yields of fluorescence

The problems associated with the accurate determination of emission quantum yields in fluorescence cells in which the emission is viewed at right angles to the exciting radiation are vexing, particularly if the emission detector scans only a

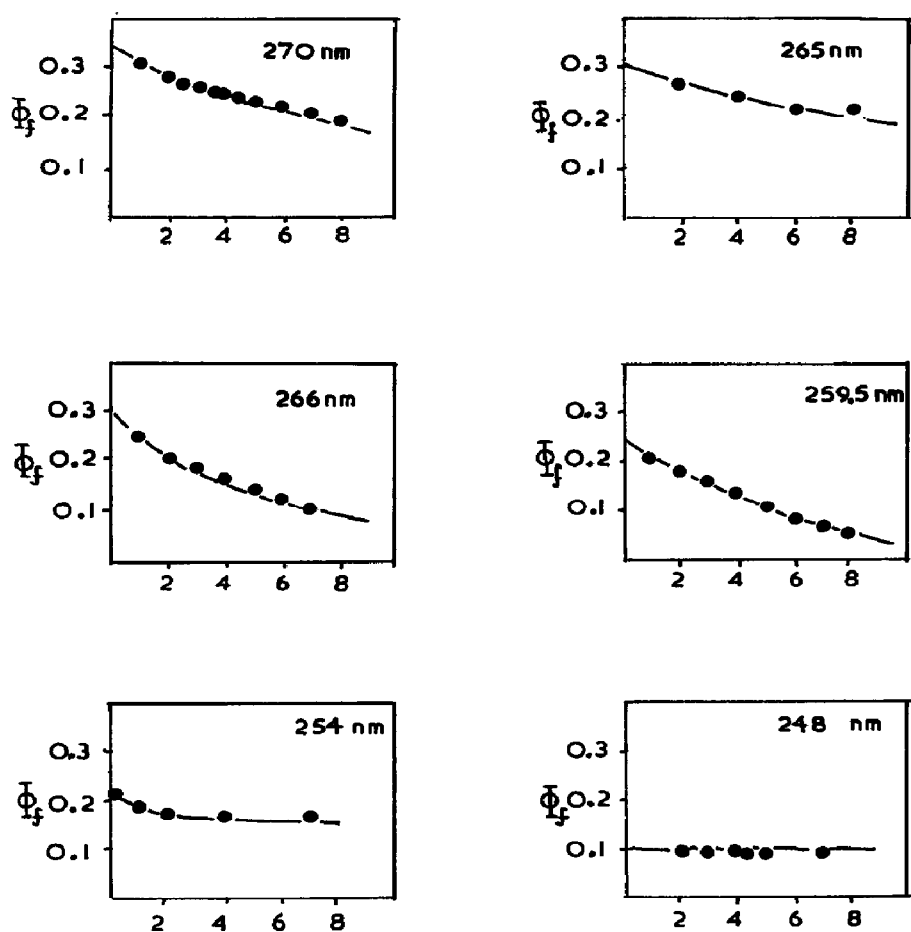


Fig. 3. Apparent variation in fluorescence quantum yield (Φ_f) of 1-fluoro-2-(trifluoromethyl) benzene with pressure of the aromatic molecule in Torr, as abscissae. Exciting wavelengths are indicated in each box.

small region of the absorption path¹⁸. Corrections to raw data may be applied using the Beer-Lambert law to calculate what fraction of the total absorption occurs in the region scanned by the emission detector, but for aromatic molecules having highly structured absorption bands, the exciting radiation generally is polychromatic with respect to the overlapping vibrational bands, and the Beer-Lambert law is inapplicable. Nevertheless, for excitation with the relatively narrow lines of a mercury arc source, an approximate correction¹⁸ may be applied which is based upon optical densities measured separately with a high-resolution spectrometer at wavelengths corresponding to the wavelength of excitation. For excitation with radiation from a xenon arc source, however, this method will lead to incorrect results.

Uncorrected results for the fluorescence quantum yield of the two fluoro, (trifluoromethyl) benzenes at different exciting wavelengths as a function of pressure of aromatic molecule are shown in Figs. 3 and 4. It is necessary to decide

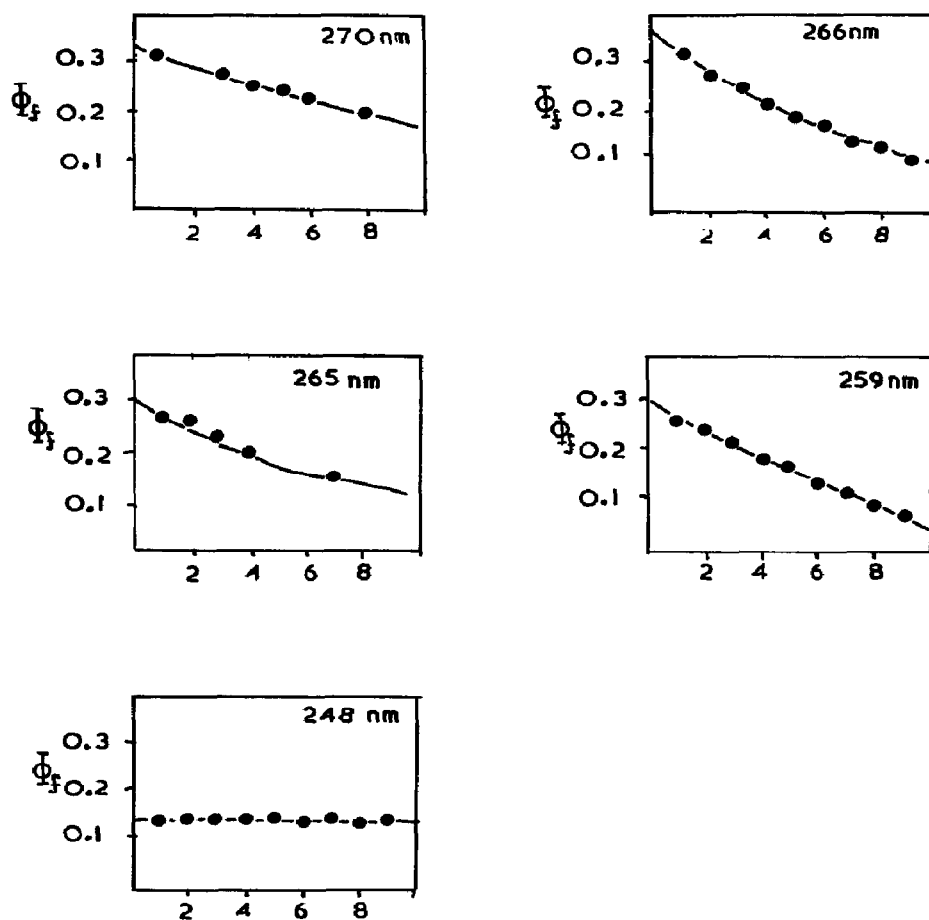


Fig. 4. Apparent variation in fluorescence quantum yield (Φ_f) of 1-fluoro-3-(trifluoromethyl) benzene with pressure of the aromatic molecule in Torr as abscissae. Exciting wavelengths are indicated in each box.

whether or not the apparent variation in quantum yield is due to self-quenching, vibrational relaxation, or an experimental artefact. Since the fluorescence decay time for excitation at 265 nm is independent of pressure of aromatic, and at the same wavelength up to 200 Torr of CF₄ or perfluorocyclobutane does not cause any variation in fluorescence quantum yield, the two real effects may be discounted. Since as discussed above it is impossible to correct the emission yield values in Figs. 3 and 4 for effect of change in optical density, the curves are all extrapolated to zero pressure, and these zero pressure values are quoted in Table 1.

TABLE 1

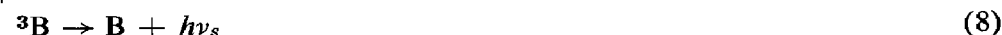
QUANTUM YIELDS OF FLUORESCENCE OF 1,2- AND 1,3-FLUORO-(TRIFLUOROMETHYL)-BENZENES*

1,2-isomer		1,3-isomer	
Exciting wavelength (nm)	Φ_f	Exciting wavelength (nm)	Φ_f
270	0.35 ± 0.03	270	0.33 ± 0.03
266	0.30 ± 0.03	266	0.36 ± 0.04
265	0.30 ± 0.03	265	0.30 ± 0.03
259.5	0.24 ± 0.02	259	0.30 ± 0.03
254	0.22 ± 0.02	248	0.14 ± 0.01
248	0.10 ± 0.01		

* Values obtained by extrapolation of curves in Figs. 3 and 4 to zero pressure.

Quantum yields of intersystem crossing

Plots of reciprocal quantum yield of sensitized phosphorescence from biacetyl (Φ_s^{-1}) as a function of pressure of biacetyl added to 2 Torr of the isomers of the aromatic molecules are shown in Figs. 5 and 6. Values of the quantum yield of intersystem crossing may be derived from these plots on the basis of the following simple mechanism:



where A is the aromatic molecule, B is biacetyl, superscripts refer to spin state, and ^{II}B represents the dissociative second excited singlet state of biacetyl. X is some other state of the aromatic.

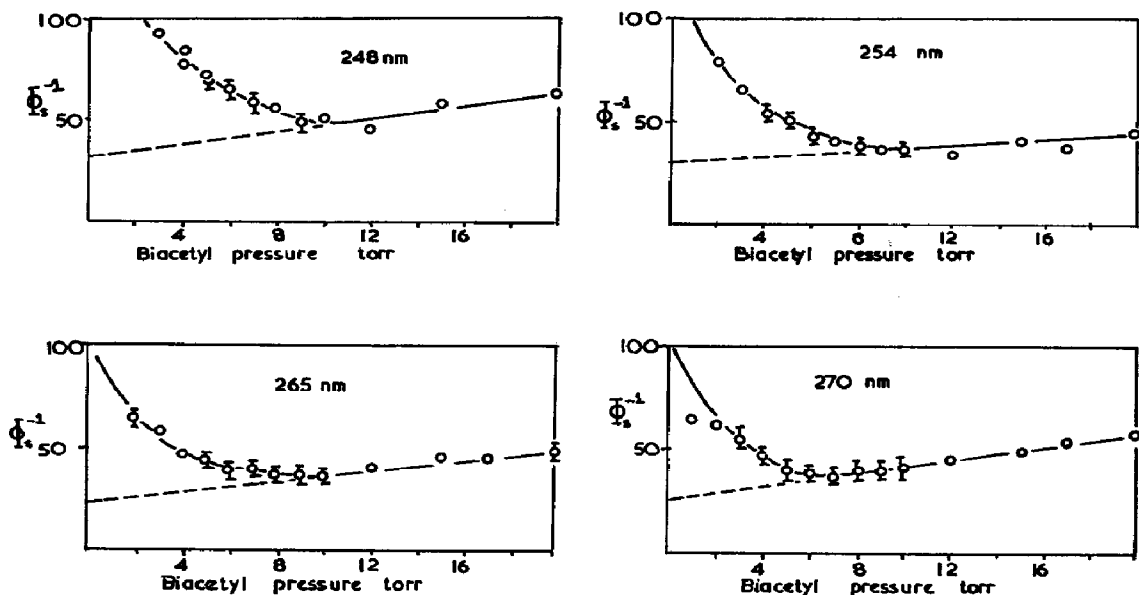


Fig. 5. Variation of reciprocal quantum yield of emission from biacetyl sensitized by 2.0 Torr 1-fluoro-2-(trifluoromethyl) benzene (Φ_s^{-1}) as a function of biacetyl pressure. Exciting wavelength shown in each box. Results consistent with these have been obtained at higher biacetyl pressures, but are omitted here.

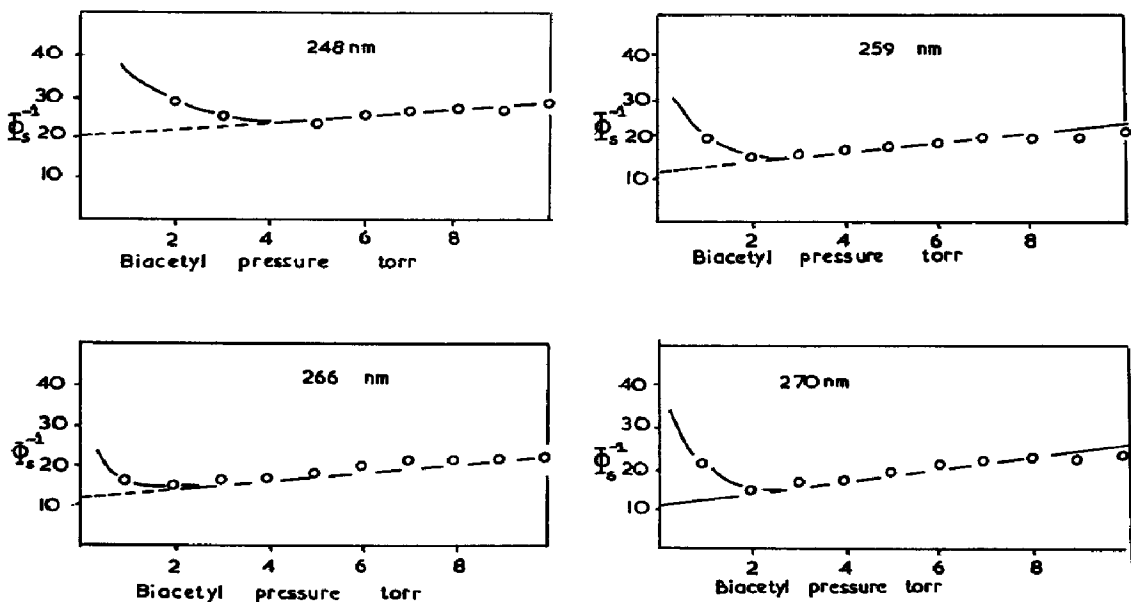


Fig. 6. Variation of reciprocal quantum yield of emission from biacetyl sensitized by 2.0 Torr 1-fluoro-3-(trifluoromethyl) benzene (Φ_s^{-1}) as a function of biacetyl pressure. Exciting wavelength shown in each box. Results consistent with these have been obtained at higher biacetyl pressures, but are omitted here.

TABLE 2
 QUANTUM YIELDS OF $S_1 - T_1$ INTERSYSTEM CROSSING IN 1,2- AND 1,3-FLUORO-(TRIFLUOROMETHYL) BENZENES

1,2-isomer		1,3-isomer					
Exciting wavelength (nm)	$(\Phi_s)_o^a$	$(\Phi_s)_o \times (\Phi_f)_o / \Phi_f^b$	$(\Phi_{ISC})_o$				
		Exciting wavelength (nm)	$(\Phi_s)_o^a$				
			$(\Phi_s)_o \times (\Phi_f)_o / \Phi_f^b$				
			$(\Phi_{ISC})_o$				
270	0.039 ± 0.008	0.047 ± 0.014	0.31 ± 0.06	270	0.097 ± 0.01	0.105 ± 0.01	0.70 ± 0.07
265	0.045 ± 0.002	0.050 ± 0.003	0.33 ± 0.02	266	0.083 ± 0.01	0.103 ± 0.01	0.69 ± 0.07
254	0.033 ± 0.003	0.039 ± 0.004	0.26 ± 0.03	259	0.080 ± 0.01	0.096 ± 0.01	0.64 ± 0.06
248	0.032 ± 0.003	0.032 ± 0.003	0.21 ± 0.02	248	0.050 ± 0.005	0.050 ± 0.005	0.33 ± 0.03

^a $(\Phi_s)_o$ values are intercepts from Figs. 5 and 6.

^b $(\Phi_s)_o / \Phi_f$ values were obtained from Figs. 3 and 4.

The expression for the reciprocal quantum yield of phosphorescence from biacetyl sensitized by the aromatic molecule (Φ_s^{-1}) is given by:

$$\Phi_s^{-1} = \left(\frac{k_8 + k_9}{k_8} \right) \left(\frac{k_6 + k_7[B]}{k_7[B]} \right) \left(\frac{k_2 + k_3 + k_4 + k_5[B]}{k_3} \right) \quad (I)$$

At high pressures of biacetyl, $k_7[B] \gg k_6$, and thus plots of Φ_s^{-1} against $[B]$ in this region are expected to be straight lines, the zero pressure intercepts of which are related to the quantum yields of intersystem crossing of the aromatic molecules [$\Phi_{ISC} = k_3 / (k_2 + k_3 + k_4)$]. Values obtained in this way are shown in Table 2, together with values corrected to zero pressure of aromatic molecule (Φ_{ISC})₀.

The 1,3-isomer exhibits the familiar behaviour that at long wavelengths the sum of quantum yields of fluorescence and intersystem crossing is within experimental error of unity. By contrast, the quantum yield of intersystem crossing in the 1,2-isomer is small, indicating that some other decay process is important in this molecule even for excitation to low vibrational levels. As the wavelength of excitation is shortened, the efficiency of the alternative non-radiative decay process is enhanced.

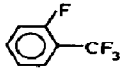
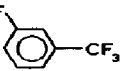
Absolute rate constants for radiative and non-radiative decay

The quantum yield measurements given in Tables 1 and 2 may be combined with fluorescence decay time data where available to yield the absolute rate constants given in Table 3. These may be compared with similar data given recently for other fluoro-substituted benzenes^{5,16,25}. It is evident that both radiative and non-radiative rate constants are an order of magnitude larger than those for benzene, and correspond to those obtained for other fluorine-substituted benzenes. It may be noted that the value of the radiative rate constant for long wavelength excitation is in both compounds a factor of two greater than that calculated by the method of integration of areas under absorption curves. The latter method works successfully for methyl-substituted benzenes, but as stated earlier, does not lead to realistic values for k_R for molecules which contain fluorine substituents. The reason for this is not at all clear, but the present results support the earlier observations that the discrepancy exists.

Loper and Lee⁷ have shown that excitation of fluorobenzene vapour to high vibrational regions of the excited singlet state causes a decrease in the rate constant for radiative decay (k_R) and an increase in the rate constant for non-radiative decay (k_{NR}), the latter being caused by the opening of a new decay channel (channel III). The results shown in Table 3 indicate that this behaviour is also seen in the two aromatic molecules studied here, in that excitation with 248 nm radiation causes a decrease in k_R and an increase in k_{NR} which is not identifiable with an intersystem crossing process.

TABLE 3

ABSOLUTE RATE CONSTANTS FOR RADIATIVE AND NON-RADIATIVE DECAY OF THE EXCITED SINGLET STATES OF 1,2- AND 1,3-FLUORO (TRIFLUOROMETHYL) BENZENES, VAPOUR PHASE, 23°C

Aromatic compound	Exciting wavelength (nm)	Φ_f^a	Φ_{ISC}^b	τ_f^c (nsec)	k_R^d $\times 10^6$ (sec ⁻¹)	k_{NR}^e $\times 10^6$ (sec ⁻¹)	k_{ISC}^f $\times 10^6$ (sec ⁻¹)
	265	0.30	0.33	8.5	35.5	38.9	82.5
	254	0.22	0.26	7.7	28.6	101.0	33.8
	248	0.10	0.21	8.9	11.3	102.0	23.6
	265	0.30	0.69	8.9	33.7	78.9	77.5
	259	0.30	0.64	9.2 ^g	32.8	76.1	69.5
	248	0.14	0.33	8.4	16.7	102.4	39.2

^a Values extrapolated to zero pressure, Table 1.

^b Values from Table 2.

^c Values from ref. 16.

^d $k_R = \Phi_f/\tau_f$.

^e $k_{NR} = (1 - \Phi_f)/\tau_f$.

^f $k_{ISC} = \Phi_{ISC}/\tau_f$.

^g Value of τ_f at 254 nm, since data not available at 259 nm.

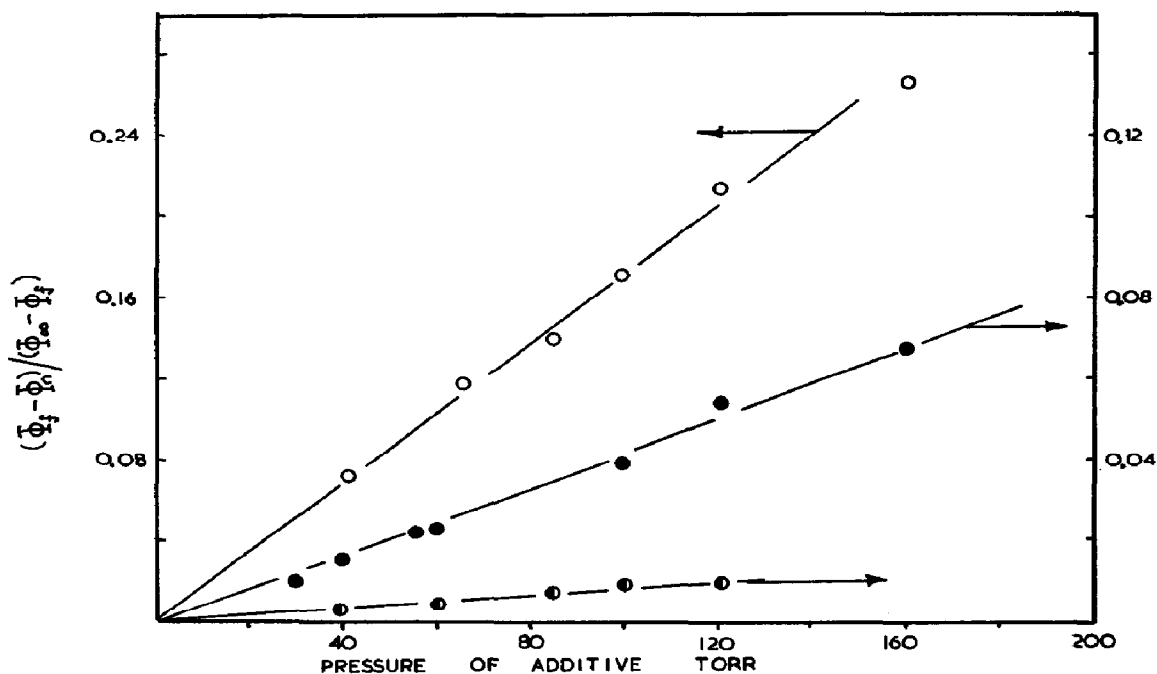


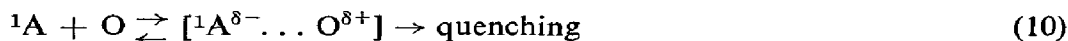
Fig. 7. Plots of $(\Phi_f - \Phi_n)/(\Phi_\infty - \Phi_f)$ against pressure of added perfluorocyclobutane, where Φ_n , Φ_∞ , and Φ_f are the quantum yields of total fluorescence at zero, infinite and any pressure of additive respectively. ● = 1,2-isomer, $\lambda_{ex.} = 248$ nm, ○ = 1,2-isomer, $\lambda_{ex.} = 254$ nm (right-hand scale). ○ = 1,3-isomer, $\lambda_{ex.} = 248$ nm (left-hand scale).

Vibrational relaxation

Upon excitation at 248 nm, the total fluorescence quantum yield of both isomers studied here is increased upon addition of the inert gas perfluorocyclobutane. A treatment has been given which shows that for a single-step deactivation process to the Boltzmann distribution of emitting levels, plots of $(\Phi_f - \Phi_n)/(\Phi_\infty - \Phi_f)$ against concentration of additive [M] should be straight lines of slope $\tau_f k_c$, where Φ_f is the total fluorescence quantum yield at any pressure [M], Φ_n that at zero pressure of additive, Φ_∞ that at infinite pressure, τ_f is the fluorescence decay time in the absence of additive, and k_c the rate constant for the collisional deactivation process²⁶. Deviations from linearity indicate a multistep relaxation process, and this has been observed for some compounds^{25, 26}. In the present case, however, the data can be satisfactorily represented by a straight line passing through the origin, as Fig. 7 indicates. Values of the rate constant for relaxation of 1-fluoro-2-(trifluoromethyl)-benzene excited at 248 nm and 254 nm by perfluorocyclobutane are 8.8×10^9 and 1.9×10^{10} l mole⁻¹sec⁻¹ respectively, and that for relaxation of the 1,3-isomer at 248 nm by the same additive 3.8×10^{10} l mole⁻¹sec⁻¹. These values are of the same order of magnitude as those obtained for relaxation of other CF₃ and F substituted benzenes^{13-15, 26}.

Quenching of the excited singlet state

The excited singlet states of the 1,2- and 1,3-isomers were found to be quenched efficiently at all wavelengths by biacetyl and pentan-2-one, and less efficiently upon excitation at 266 nm by buta-1,3-diene and *cis*-but-2-ene. Stern-Volmer plots of (Φ_{f0}/Φ_f) against pressure of additive are shown in Figs. 8-10, and rate constant data derived from these are given in Table 4. The data for the olefins support the contention that an incipient charge-transfer interaction is the mechanism of quenching by olefins, [O], which may precede chemical interaction,



Thus the efficiency of quenching of the singlet states of these aromatic molecules is significantly in excess of that of benzene, fluorobenzene, or (trifluoromethyl)-benzene. Fluorine substitution increases the electron affinity of the benzene moiety by approximately 0.4 eV per substituent²⁷, and CF₃ substitution has this property to an even more pronounced degree (~ 1.0 eV)²⁸. Increase in electron affinity of the aromatic molecule should therefore lead to enhancement in the quenching rate by the mechanism above, as is observed experimentally.

The large cross-sections observed for quenching by the ketonic species suggests that Forster long-range energy transfer may contribute to the overall efficiency, as has been suggested for other donor-acceptor pairs recently¹⁷. Were this the case, quenching cross-sections should correlate with radiative rate constant of donor, assuming equal overlap of fluorescence spectra of donors and absorption spectra of acceptors. This appears to be the case in the present experiments, since

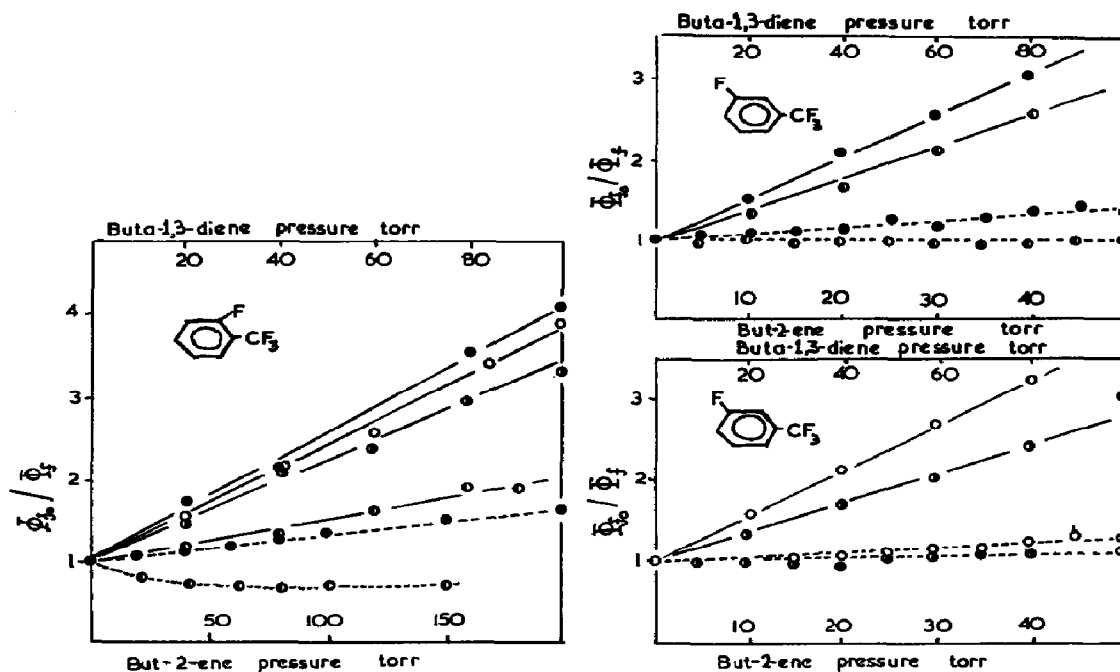


Fig. 8. Stern-Volmer plots of Φ_{f0}/Φ_f , where Φ_{f0} is quantum yield of fluorescence of aromatic molecule at zero pressure of additive, and Φ_f that at any pressure, against pressure of additive for quenching of excited singlet states of 1,2- and 1,3-isomers by olefins. —, olefin = buta-1,3-diene (top scale). - - - - -, olefin = *cis*-but-2-ene (bottom scale). \circ = λ_{ex} 270 nm; \bullet = λ_{ex} 266 nm; \odot = λ_{ex} 259 nm; \odot = λ_{ex} 248 nm; \bullet = λ_{ex} 265 nm. The results for but-2-ene excited at 248 nm show an almost negligible slope for the 1,3-isomer, and a negative curvature for the 1,2-isomer, indicating that the olefin molecule is acting principally as a vibrational relaxer under these conditions.

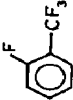

the donors have higher radiative transition probabilities (oscillator strengths) than any of the other substituted benzenes studied to date, and similarly large cross-sections are observed.

Quenching of the excited triplet states

But-2-ene quenches the excited triplet states of both aromatic isomers, although relatively inefficiently compared with that of other substituted benzenes. This was shown by the quenching of the phosphorescence of biacetyl sensitized by the aromatic upon addition of *cis*-but-2-ene. Since at the pressures of but-2-ene necessary to observe triplet quenching some singlet quenching also is observed, plots of Φ_f/Φ_s are necessary to extract the triplet quenching data shown in Table 5. Such plots are given in Fig. 11. Thus, for the competing reactions:



TABLE 4
 QUENCHING PARAMETERS FOR THE EXCITED SINGLET STATES OF 1,2- AND 1,3-FLUORO(TRIFLUOROMETHYL) BENZENE

Aromatic compound	Quencher	λ_{ex} (nm)	Slope ^a $\times 10^{-2}$ (Torr ⁻¹)	τ_f^b (nsec)	k_Q $\times 10^{10}$ (l mole ⁻¹ sec ⁻¹)	σ^{de} $\times 10^{-16}$ (cm ²)	
	<i>cis</i> -But-2-ene	266	0.375	8.5	0.82 ± 0.04	1.1 ± 0.05	
	Buta-1,3-diene	270	2.95	8.5 ^d	6.4 ± 0.3	8.8 ± 0.4	
	Buta-1,3-diene	266	3.15	8.5	6.9 ± 0.3	9.4 ± 0.5	
	Buta-1,3-diene	259	2.55	7.7 ^e	6.3 ± 0.3	8.5 ± 0.4	
	Buta-1,3-diene	248	1.1	8.9	2.3 ± 0.1	3.1 ± 0.2	
	Biacetyl	270	15.5	8.5 ^d	33.9 ± 1.5	56 ± 3	
	Biacetyl	266	12.5	8.5	27.3 ± 1.4	45 ± 2	
	Biacetyl	259	9.0	7.7 ^e	22.1 ± 1.1	36 ± 2	
	Biacetyl	248	6.5	8.9	13.6 ± 0.7	22 ± 1	
	Pentan-2-one	270	16.0	8.5 ^d	35.0 ± 1.7	57 ± 3	
	Pentan-2-one	266	15.0	8.5	32.8 ± 1.6	54 ± 3	
	Pentan-2-one	259	8.4	7.7 ^e	20.3 ± 1.0	33 ± 2	
	Pentan-2-one	248	8.4	8.9	17.5 ± 0.9	29 ± 2	
		<i>cis</i> -But-2-ene	270	0.66	8.9 ^d	1.4 ± 0.1	1.9 ± 0.1
		<i>cis</i> -But-2-ene	266	0.80	8.9	1.7 ± 0.1	2.3 ± 0.1
		<i>cis</i> -But-2-ene	259	0.32	9.2 ^e	0.64 ± 0.06	0.87 ± 0.04
Buta-1,3-diene		270	2.80	8.9 ^d	5.9 ± 0.3	7.9 ± 0.4	
Buta-1,3-diene		266	2.55	8.9	5.3 ± 0.2	7.2 ± 0.3	
Buta-1,3-diene		259	1.8	9.2 ^e	3.6 ± 0.1	4.9 ± 0.2	
Buta-1,3-diene		248	1.95	8.4	4.3 ± 0.2	5.9 ± 0.3	
Biacetyl		270	15.75	8.9 ^d	32.9 ± 1.6	54 ± 3	
Biacetyl		266	12.75	8.9	26.6 ± 1.3	44 ± 2	
Biacetyl		259	10.25	9.2 ^e	20.7 ± 1.0	34 ± 2	

Biacyl	248	7.5	8.4	16.5 ± 0.8	27 ± 1
Pentan-2-one	270	16.75	8.9 ^d	34.9 ± 1.7	57 ± 3
Pentan-2-one	266	14.25	8.9	29.8 ± 1.5	49 ± 2
Pentan-2-one	259	9.85	9.2 ^e	19.9 ± 1.0	32.5 ± 2
Pentan-2-one	248	8.25	8.4	18.3 ± 0.9	30 ± 1

^a From Figs. 8, 9, and 10.

^b From ref. 16.

^c From relationship $\sigma^2 = kQ (8\pi kT/\mu)^{1/2}$.

^d Assumed value.

^e Value for $\lambda_{\text{ex}} = 254 \text{ nm}$.

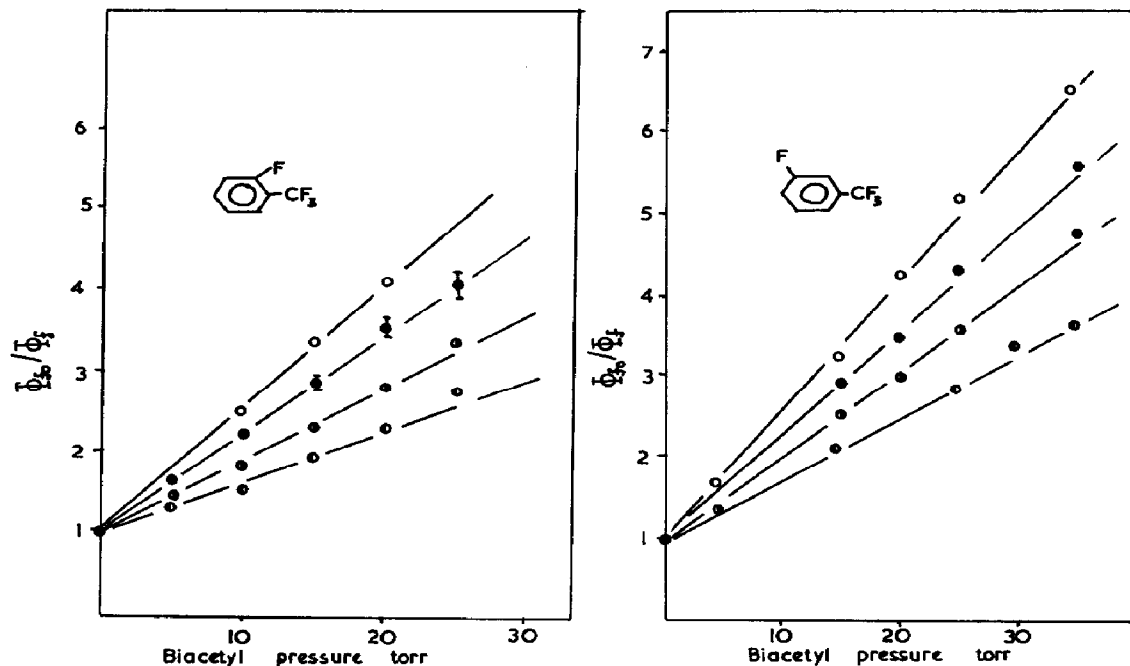


Fig. 9. Stern-Volmer plots for quenching of fluorescence of the aromatic isomers by biacetyl. Symbols as for Fig. 8.

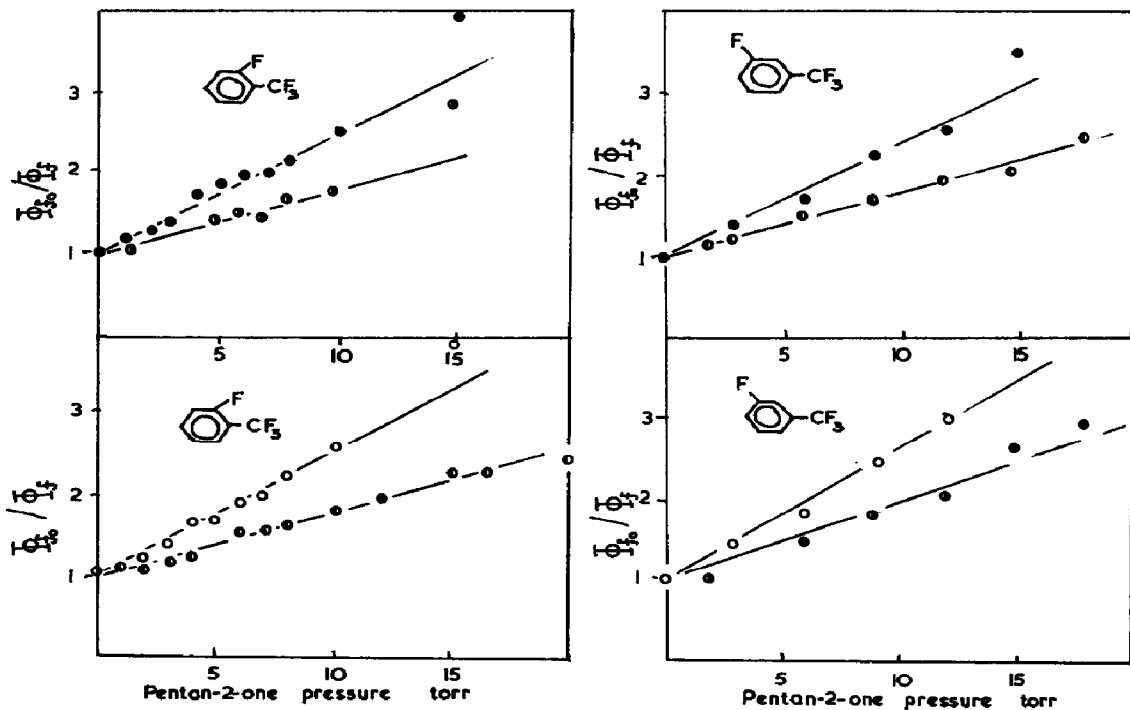
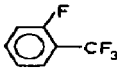
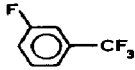

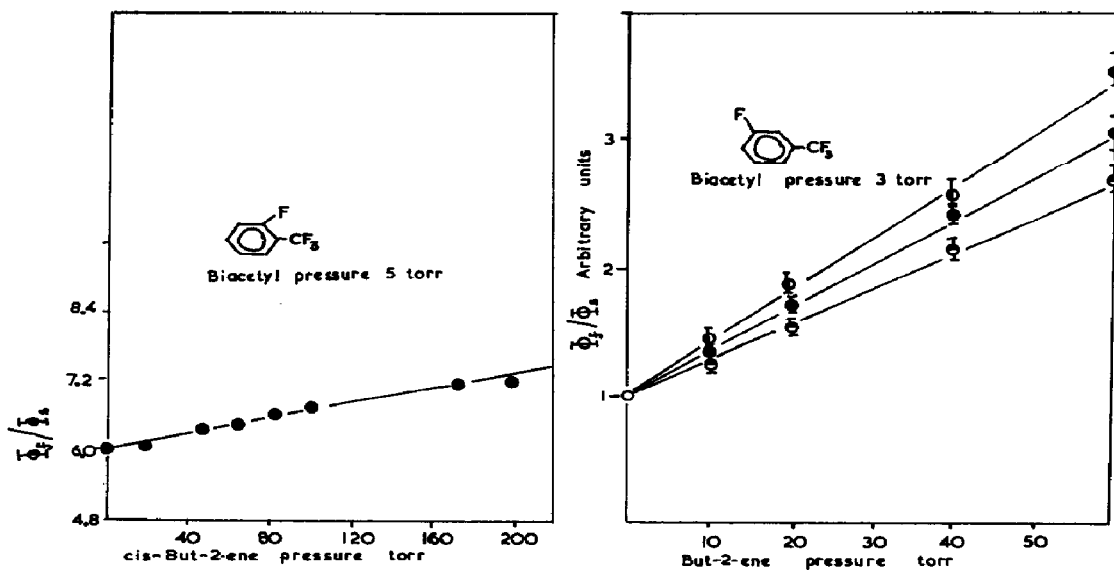


Fig. 10. Stern-Volmer plots for quenching of fluorescence of the aromatic isomers by pentan-2-one. Symbols as for Fig. 8. At high pressures of added pentan-2-one, deviations from linearity occur due to absorption by the ketone itself of some of the exciting radiation. These results were thus rejected.

TABLE 5

COMPETITIVE QUENCHING OF 1,2- AND 1,3-FLUORO(TRIFLUOROMETHYL) BENZENE TRIPLET STATES BY BIACETYL AND OLEFINS

Aromatic compound	Quencher	λ_{ex} (nm)	k_0/k_B^a (Torr $^{-1}$)	Biacetyl pressure (Torr)	k_0/k_B
	<i>cis</i> -But-2-ene	266	1.18×10^{-3}	5.0	5.5×10^{-3}
	Buta-1,3-diene	270	4.5	7.5	33.8
	Buta-1,3-diene	265	5.0	7.5	37.5
	Buta-1,3-diene	259.5	5.25	7.5	38.2
	Buta-1,3-diene	248	6.0	7.5	45.0
	But-2-ene	265	3.61×10^{-2}	3.0	0.11
	But-2-ene	254	2.95×10^{-2}	3.0	0.09
	But-2-ene	248	4.15×10^{-2}	3.0	0.12
	Buta-1,3-diene	266	9.0	2.5	22.5
	<i>cis</i> -But-2-ene	254	—	—	0.263 ^b
	Buta-1,3-diene	254	—	—	5.46 ^b

^a Slope/intercept from Fig. 11, or slope from Fig. 12.^b Values from G. A. Haninger Jr. and E. K. C. Lee, *J. Phys. Chem.*, 73 (1969) 1815.,Fig. 11. Plots of Φ_f/Φ_s against pressure of added but-2-ene. Symbols as in Fig. 8. Φ_f and Φ_s are as defined above. For the 1,3-isomer, both *cis* and *trans*-but-2-ene were used, and no difference in the results noticed.

it can be shown that:

$$\Phi_f/\Phi_s = \frac{(k_8 + k_9)}{k_8} \times \frac{k_2}{k_3} \times \left[1 + \frac{k_0}{k_B} \frac{[O]}{[B]} \right] \quad (\text{II})$$

Thus the ratio of slope to intercept in Fig. 11 gives a measure of the rate constant ratio, k_0/k_B . In the absence of information on the triplet lifetimes of the aromatic molecules, no absolute rate constants can be quoted. The ratio for the 1,2-isomer is, however, significantly lower than that in benzene, indicating either an enhancement of the energy transfer rate to biacetyl, or reduction in transfer rate to but-2-ene, or both, compared with the benzene system. Phosphorescence data indicate that the energy levels of the triplet states of both aromatic isomers under investigation to be similar (3.61 and 3.70 eV for the 1,2- and 1,3-isomers, respectively)²⁵

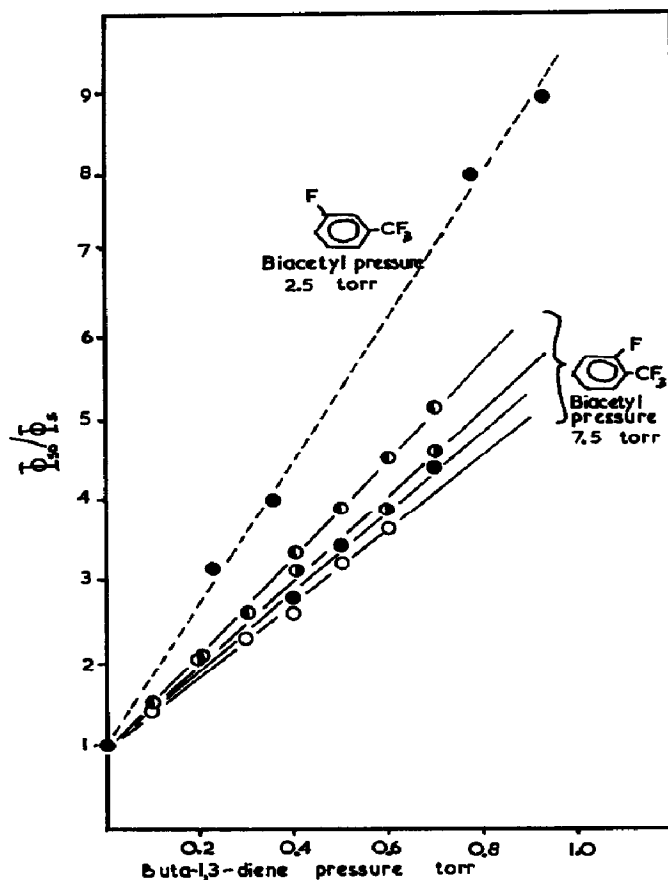


Fig. 12. Plots indicating the quenching of the excited triplet states of the aromatic isomers by buta-1,3-diene. Since no significant singlet state quenching occurs at the pressures of olefin added, the results are shown in the form of plots of Φ_{so}/Φ_s where Φ_{so} is the quantum yield of sensitized emission in the absence of olefin, and Φ_s that at any pressure. Rate constants are obtained from the relationship $\Phi_{so}/\Phi_s = 1 + k_0 [O]/k_B [B]$ where k_0 and k_B are as defined in text.

and not much different from that of benzene (3.68 eV). This is significantly higher than that of but-2-ene (3.4 eV)²⁹, and thus the apparent reduction in transfer efficiency with respect to benzene is unlikely to be associated with energy levels alone. For the exchange energy transfer mechanism proposed, the magnitude of the normalized overlap between emission of donor (phosphorescence) and absorption of acceptor (singlet to triplet absorption) is critical in determining transfer efficiency. In the absence of detailed information of this type, no predictions as to relative efficiency can be made, except to note that the phosphorescence maxima of the two isomers is shifted to longer wavelengths with respect to that of benzene, and thus some differences in efficiencies are to be expected. Differences in the behaviour of the two isomers with respect to triplet quenching by butadiene are less pronounced, as shown in Fig. 12 and Table 5.

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