

SUBSTITUENT EFFECTS IN THE PHOTOCHEMISTRY OF BENZENE VAPOUR

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INTRODUCTION

Benzene has long been considered the prototype aromatic molecule as far as its spectroscopy is concerned and perhaps for this reason the photochemistry and photophysics of the electronically excited states of benzene continue to be subjects which are being actively studied. In condensed media, the rates of photoprocesses may be affected greatly by the presence of the surrounding matrix, and thus the properties of the isolated free molecule may only be studied in the vapour phase at low pressures. Under such conditions not only can the radiative and non-radiative properties of the unperturbed molecule be determined, but by excitation with

TABLE 1
ENERGY LEVELS OF METHYL-SUBSTITUTED BENZENES

Compound	Observed eV				Calculated eV				Ref.			
	S ₁	S ₂	T ₁	S ₃	S ₁	S ₂	S ₃	T ₁		T ₂	T ₃	T ₄
Benzene (∅)	4.71 ³	5.96 ²	3.68 ²	(5.96)	(4.71)	(6.75)	(6.75)	(3.68)	(4.53)	(4.53)	(4.71)	2
Me-∅	4.62 ³	—	3.58 ²	5.85	4.60	6.64	6.67	3.60	4.28	4.45	4.1	1
	4.65 ^{1a}	5.77 ^{1a}	—	—	—	—	—	3.56	—	—	—	2
1,2-diMe-∅	4.56 ³	—	3.55 ²	5.72	4.52	6.50	6.59	3.54	4.18	4.39	4.73	1
	4.62 ^{1a}	5.72 ^{1a}	—	—	—	—	—	3.55	—	—	—	2
1,3-diMe-∅	4.55 ³	—	3.48 ²	5.82	4.51	6.47	6.55	3.54	4.18	4.39	4.73	1
	4.58 ^{1a}	5.65 ^{1a}	—	—	—	—	—	3.49	—	—	—	2
1,4-diMe-∅	4.51 ³	5.58 ²	3.48 ²	5.66	4.44	6.54	6.66	3.51	3.98	4.39	4.98	1
	4.55 ^{1a}	5.60 ^{1a}	—	—	—	—	—	3.48	—	—	—	2
1,2,3-triMe-∅	4.57 ^{1a}	—	—	5.66	4.47	6.31	6.48	3.48	4.27	4.32	4.47	1
	4.50 ^{3a}	5.64 ^{1a}	—	—	—	—	—	—	—	—	—	—
	4.53 ^{1a}	5.56 ^{1a}	—	—	—	—	—	—	—	—	—	—
1,2,4-triMe-∅	4.55 ³	—	3.47 ²	5.61	4.39	6.38	6.53	3.46	3.97	4.31	4.83	1
	4.53 ^{1a}	5.55 ^{1a}	—	—	—	—	—	3.47	—	—	—	2
1,3,5-tri-Me-∅	4.55 ³	—	3.47 ²	5.82	4.47	6.29	6.42	3.48	4.27	4.32	4.47	1
	4.53 ^{1a}	5.55 ^{1a}	—	—	—	—	—	3.43	—	—	—	2
1,2,3,4-tetraMe-∅	4.51 ^{1a}	5.56 ^{1a}	—	5.53	4.37	6.20	6.40	3.41	4.08	4.20	4.58	1
	—	—	—	—	—	—	—	—	—	—	—	—
1,2,3,5-tetraMe-∅	4.50 ^{1a}	5.51 ^{1a}	3.45 ²	5.62	4.36	6.23	6.36	3.42	4.04	4.25	4.57	1
	—	—	—	—	—	—	—	3.43	—	—	—	—
1,2,4,5-tetraMe-∅	4.49 ^{1a}	5.53 ^{1a}	3.46 ²	5.51	4.27	6.31	6.40	3.40	3.81	4.27	4.82	1
	—	—	—	—	—	—	—	3.46	—	—	—	2
Penta-Me-∅	4.47 ^{1a}	5.48 ^{1a}	3.44 ²	5.46	4.30	6.11	6.27	3.35	3.97	4.18	4.50	1
	—	—	—	—	—	—	—	3.40	—	—	—	2
Hexa-Me-∅	—	—	3.45 ^{2b}	5.38	4.26	5.98	6.15	3.30	4.05	4.13	4.26	1

TABLE 2
ENERGY LEVELS OF FLUORINE-SUBSTITUTED BENZENES

Compound	Observed eV			Calculated eV							Ref.	
	S ₁	S ₂ ^f	T ₁	S ₁	S ₂	S ₃	S ₄	T ₁	T ₂	T ₃		T ₄
Benzene (∅) F-∅	4.71	5.96	3.68	(4.71)	(5.96)	(6.75)	(6.75)	(3.68)	(4.53)	(4.53)	(4.71)	—
	4.66 ^a	5.79	3.55 ^g	4.56	5.90	6.67	(6.75)	3.61	4.13	4.46	4.99	1
	4.69 ^g	—	3.66 ¹²¹	4.84	6.09	6.93	6.95	—	—	—	—	7
	4.69 ^{1a}	—	—	4.49	—	—	—	—	—	—	—	8
1,2-diF-∅	4.66 ^a	5.79	3.59 ^g	4.48	5.75	6.53	6.72	3.56	4.04	4.41	4.92	1
	—	—	—	4.78	5.98	5.83	6.85	—	—	—	—	7
	—	—	—	4.38	—	—	—	—	—	—	—	8
1,3-diF-∅	4.68 ^a	5.83	3.26 ^g	4.48	5.94	6.52	6.61	3.56	4.04	4.41	4.92	1
	4.70 ¹⁰	—	—	4.79	6.01	6.83	6.86	—	—	—	—	7
	4.67 ^{1a}	—	—	4.40	—	—	—	—	—	—	—	8
	4.46 ^a	5.83	3.45 ^g	4.28	5.70	6.31	6.59	3.54	3.67	4.41	5.35	1
1,4-diF-∅	4.57 ¹¹	—	—	4.76	5.99	6.88	6.93	—	—	—	—	7
	4.57 ^{1a}	—	—	4.41	—	—	—	—	—	—	—	8
	—	—	—	—	—	—	—	—	—	—	—	—
1,2,3-triF-∅	—	—	3.65 ^{14a}	4.49	5.70	6.31	6.59	3.50	4.29	4.35	4.49	1
	—	—	3.61 ^{14b}	4.74	5.90	6.72	6.74	—	—	—	—	7
	—	—	—	4.36	—	—	—	—	—	—	—	8
1,2,4-triF-∅	4.59 ^a	5.80	3.4 ^g	4.27	5.65	6.38	6.72	3.48	3.69	4.33	5.16	1
	4.60 ^{1a}	—	3.62 ^{14a}	4.71	5.91	6.77	6.81	—	—	—	—	7
	4.60 ^{1a}	—	3.65 ^{14b}	4.24	—	—	—	—	—	—	—	8
	4.56 ^a	5.61	3.44 ^g	4.49	6.04	6.28	6.46	3.50	4.29	4.35	4.49	1
1,3,5-triF-∅	4.78 ^{1a}	—	3.72 ^{14a}	4.75	5.96	6.76	6.76	—	—	—	—	7
	4.78 ^{1a}	—	3.70 ^{14b}	4.40	—	—	—	—	—	—	—	8
	4.69 ^a	5.52	3.35 ^g	4.34	5.53	6.14	6.53	3.43	3.94	4.21	4.77	1
1,2,3,4-tetraF-∅	—	—	—	4.68	5.83	6.65	6.68	—	—	—	—	7
	—	—	—	4.23	—	—	—	—	—	—	—	8
	—	—	—	—	—	—	—	—	—	—	—	—

Table 2 (continued)

Compound	Observed eV			Calculated eV						Ref.		
	S ₁	S ₂ ⁵	T ₁	S ₁	S ₂	S ₃	S ₄	T ₁	T ₂		T ₃	T ₄
1,2,3,5-tetraF-Ø	4.71 ⁴	5.58	3.26 ⁶	4.31	5.70	6.23	6.43	3.44	3.88	4.27	4.75	1
	—	—	—	4.68	5.85	6.68	6.69	—	—	—	—	7
	—	—	—	4.22	—	—	—	—	—	—	—	8
1,2,4,5-tetraF-Ø	4.52 ⁴	5.70	3.49 ⁶	4.08	5.52	6.32	6.58	3.42	3.48	4.29	5.19	1
	4.54 ^{1a}	—	—	4.65	5.83	6.72	6.74	—	—	—	—	7
	4.54 ^{1a}	—	—	4.14	—	—	—	—	—	—	—	8
1,2,3,4,5-pentaF-Ø	4.46 ⁴	5.31	3.31 ⁶	4.24	5.46	6.07	6.30	3.36	3.80	4.20	4.67	1
	—	—	—	4.63	5.77	6.61	6.61	—	—	—	—	7
	—	—	—	4.14	—	—	—	—	—	—	—	8
hexaF-Ø	4.28 ⁴	4.96	3.22 ⁶	4.25	5.34	5.82	6.14	3.30	4.02	4.15	4.25	1
	—	—	—	4.59	5.71	6.54	6.54	—	—	—	—	7
	—	—	—	4.14	—	—	—	—	—	—	—	8

narrow bandwidth light sources the effects of preparation of the excited molecule with different initial distributions of vibrational energy upon these photoprocesses may also be investigated. Benzene itself has been the subject of several intensive studies of this type recently, and it is the purpose of this article to review these recent advances in the understanding of the benzene molecule, and to compare the photochemistry of the parent molecule with molecules in which a simple substituent group has been introduced into the aromatic ring. The substituent groups discussed are the methyl, fluoro, and trifluoromethyl upon which considerable work has been done, plus several other miscellaneous substituents.

Higher triplet states may be observed in flash photolysis experiments in which triplet-triplet absorption is measured, but generally the states observed in such experiments are very much higher in energy than the lowest triplet state. Since triplet states intermediate in energy between the lowest singlet and triplet states may play a crucial role in determining the overall rate of the $S_1 \rightarrow T_1$ intersystem crossing process, and these are not observable experimentally, molecular orbital calculations may prove to be of use in gaining an approximate idea of the relative energies of these intermediate states.

In Tables 1, 2, and 3 the available data, both experimental and calculated, on the energy levels of the CH_3 , F, CF_3 and other substituted benzenes respectively are summarized. It is evident from these Tables that the fluorine substituent has the largest perturbing effect upon the positions of the benzene excited states. The localized orbital molecular orbital calculations¹ carried out upon the fluoro-benzenes are seen to be an improvement upon the simple Huckel calculations for this series⁸, but it is evident from the results obtained by this method for the methyl benzenes that refinement is necessary before accurate results can be obtained.

The energy levels will be discussed later in the sections dealing with quenching the excited states.

TABLE 3

ENERGY LEVELS OF CF_3 AND OTHER SUBSTITUTED BENZENES (EXPERIMENTAL)

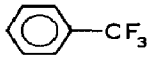
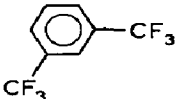

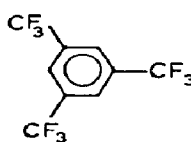
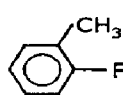
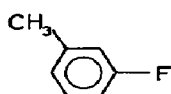
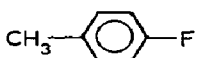
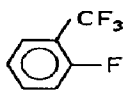
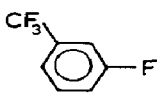
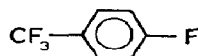
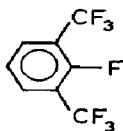
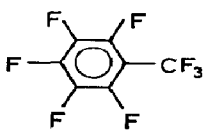
Compound	S_1	S_2^a	T_2^b	Reference
	{ 4.61 4.69	5.58 —	3.62 —	4, 5, 6 15
	4.61	5.53	3.59	4, 5, 6
	{ 4.44 4.64, 4.64	— —	3.44 —	3a, 6 4, 15a

Table 3 (continued)

Compound	S_1	S_2^a	T_2^b	Reference
	4.72	—	—	16b
	4.59	—	3.42	4, 6
	4.59	—	3.54	4, 6
	4.51	—	3.47	4, 6
	4.70a 4.56b	—	3.61	17, 6
	4.63	—	3.70	18, 6
	4.69	—	—	18
	4.56	—	—	19
	4.67	—	—	19

^a Energy corresponding to absorption coefficient 10% of maximum on long wavelength side.

^b From phosphorescence spectra, ± 0.05 eV, accuracy.

ENERGY LEVELS OF SUBSTITUTED BENZENES

Since the rates of non-radiative transitions between states of the molecules under consideration may be critically dependent upon the energy differences between adjacent states, and also quenching parameters especially for triplet states may depend upon the triplet energy of the molecules, it is desirable to know the energies of the excited singlet and triplet states of the substituted molecules. The energy of the first excited singlet state may be fairly readily fixed by an analysis of the vibrational structure of the first absorption band, and thus zero-zero transitions for most simply substituted benzenes are known with a high degree of accuracy. Absorption to second, and higher singlet states, however, does not usually give rise to structured spectra, and thus the position of the second and higher singlet states can only be estimated by determining the onset of absorption. Since this depends rather arbitrarily upon the concentration of the species being investigated, the precision with which energy levels of higher excited singlet states are known is rather less than that for first singlet levels. The energy levels of lowest triplet states are not usually amenable to experiments in the gas phase, but may be determined by examination of phosphorescence spectra in the solid phase, usually at 77 K, and by enhancement of ground-state to triplet state absorption by molecular oxygen perturbation, for example. It is questionable whether these techniques yield results which relate to the situation in the vapour phase, but in the absence of other data they provide the only experimental evidence available concerning these states.

QUANTUM YIELDS OF FLUORESCENCE

Fluorescence quantum yields for many substituted benzenes in the vapour phase have been measured, usually using benzene vapour as a standard²⁰. This in itself gives rise to a difficulty in that it has been shown that excitation of benzene vapour at 2537 Å followed by collisional relaxation produces a wide distribution of emitting levels²¹⁻²³. In order to compare the effects of different substituents upon the rates of the decay processes, it is essential that quantum yields be compared which are characteristic of an identifiable vibrational level of the excited singlet state, namely the zeroth vibrational level. Although benzene vapour has itself been studied under conditions such that the zeroth vibrational level alone is populated (by absorption from a hot band in the ground state), and such that no collisions with surrounding molecules occur before emission²³, these ideal conditions have not usually been met in the studies upon the substituted benzenes*. Since, however, radiative lifetimes of the substituted benzenes are usually considerably shorter than that of benzene, there are enough data in the literature at moderate pressures to extract relevant information. However, in few cases have

* See notes added in proof on page 146.

zero-zero transitions been excited, and thus for the sake of comparison, the data tabulated below are those obtained at exciting wavelengths closest to the zero-zero transition.

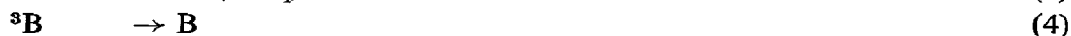
It should be stressed that the accuracy of quantum yield data for fluorescence is limited, due to difficulties in correction of raw data for experimental conditions such as widebandpass excitation²⁴, effect of geometry of the fluorescence cell etc, but the results included in Tables 4, 5 and 6 and 7 for the methyl, fluoro and trifluoromethyl, and mixed substituent groups are probably accurate to better than 10%.

QUANTUM YIELDS OF $S_1 \rightarrow T_1$ INTERSYSTEM CROSSING

Since the lowest triplet state of benzene, the $^3B_{1u}$ state is not phosphorescent in the vapour phase, and exhibits only weak triplet-triplet absorption measurement of quantum yields of $S_1 \rightarrow T_1$ intersystem crossing must rely upon other methods. Two techniques have been widely employed for this purpose, those of the sensitization of emission from biacetyl vapour²⁵, and the sensitization of the *cis-trans* isomerization of but-2-ene^{26,27}, and these techniques have generally been used to obtain the data given in Tables 4-7. Some comments about the techniques and limits of accuracy obtained are in order. Both methods rely upon the transfer of electronic energy by a collisional exchange mechanism from the aromatic triplet state to the added quencher, and it is usually assumed throughout that the aromatic triplet state in the absence of quencher decays by a first order process (1). Upon addition of the quencher, say biacetyl (B), process (2),



where A is the aromatic molecule competes with reaction (1), and the fate of the excited biacetyl triplet state is either phosphorescence (3) or intersystem crossing to the ground state:



Since $k_3/(k_3 + k_4)$ is known from experiments in which biacetyl is excited directly²⁸, it can be seen that provided a sufficiently high pressure of biacetyl can be added such that reaction (1) is suppressed entirely, then measurement of the limiting quantum yield of phosphorescence of biacetyl sensitized by the aromatic (Φ_s) can be used to extract the value of the quantum yield of formation of the triplet state of the aromatic molecule, Φ_{isc} thus,

$$(\Phi_s)_{lim} = \Phi_{isc} \cdot k_3/(k_3 + k_4) \quad (I)$$

However, this treatment does not take into account the possibility of the excited singlet state of the aromatic being quenched by the biacetyl, and since this appears

TABLE 4
RATE PARAMETERS FOR PHOTOPROCESSES IN METHYL (CH₃) SUBSTITUTED BENZENES, VAPOUR PHASE

Positions of substituents	Pressure (torr)	Exciting wavelength (nm)	Φ_f	Φ_{isc}	Decay time, τ (ns)	τ_R (ns)	τ_R (calc.) ^a (ns)	k_R 10 ⁶ (s ⁻¹)	k_{NR} 10 ⁶ (s ⁻¹)	k_{isc} 10 ⁶ (s ⁻¹)	Point group
0	20	254	0.18 ²⁰	0.72 ⁵⁶	77 ⁵⁶	428	407	2.33	10.6	9.3	D _{6h}
1	3.5-18	264	0.30 ⁵⁶	0.70 ⁵⁶	56 ⁵³	180	141	5.36	12.5	12.5	C _{2v}
1,2	3-5.5	270	0.38 ⁵⁷	0.53 ³⁷	52 ⁵³	136	152	7.31	11.9	10.2	C _{2v}
1,3	3	271	0.35 ⁵⁷	0.40 ³⁷	49 ⁵³	140	167	7.14	13.3	8.2	C _{2v}
1,4	3	272	0.52 ⁵⁷	0.54 ³⁷	44 ⁵³	85	95	11.8	10.9	12.2	D _{6h}
1,2,3	1-2	270	(0.29) ^b	—	70 ⁵³	—	238	(4.2) ^c	(10.6) ^d	—	C _{2v}
1,2,4	1.8	270	(0.55) ^b	—	40 ⁵³	—	72	(13.8) ^c	(11.2) ^d	—	C _s
1,3,5	1.5-1.8	272	(0.24) ^b	—	54 ⁵³	—	222	(4.49) ^e	(14.1) ^d	—	D _{6h}
1,2,3,4	0.04	280	(0.31) ^b	—	64 ⁵³	—	206	(4.8) ^c	(11.9) ^d	—	C _{2v}
1,2,3,5	0.05	277	(0.36) ^b	—	68 ⁵³	—	187	(5.3) ^c	(9.4) ^d	—	C _{2v}
1,2,4,5	0.03	280	(0.52) ^b	—	37 ⁵³	—	71	(14.1) ^c	(13.0) ^d	—	D _{6h}
1,2,3,4,5	0.015	277	(0.25) ^b	—	54 ⁵³	—	217	(4.6) ^c	(13.8) ^d	—	C _{2v}
1,2,3,4,5,6	—	—	—	—	—	—	312	(3.2) ^e	—	—	D _{6h}

^a Value calculated by one of methods of integration of area under absorption curve (see refs. 43, 44).

^b No measured value, value quoted is $(\tau_R)_{calc}/\tau$.

^c Values given are $(\tau_R)^{-1}_{calc}$.

^d Values given are $k_R \{(1-\Phi_f)/\Phi_f\}$.

TABLE 5

RATE PARAMETERS FOR PHOTOPROCESSES IN FLUORINE (F) SUBSTITUTED BENZENES, VAPOUR PHASE

Positions of substituents	Pressure (torr)	Exciting wavelength (nm)	Φ_f	Φ_{isc}	Decay time, τ (ns)	τ_R (ns)	τ_R (calc.) ^a (ns)	τ_{NR} (ns)	(k_R) calc. 10^9 (s^{-1})	(k_{isc}) calc. 10^8 (s^{-1})	Point group
0	20	254	0.18 ²⁰	0.72 ⁵⁵	77 ⁴⁶	428	407	94	2.45	9.80	D _{6v}
1	1.0	265	0.22 ⁵⁸	0.82 ³⁴	9.5 ⁵⁹	43	110	12.2	8.69	32.4	C _{2v}
1	3	267	0.25 ⁶⁰	0.57 ⁶¹	9.5 ⁵⁹	38	—	12.7	8.69	19.8	C _{2v}
1,2	1-6	266	0.15 ⁶²	0.71 ⁶²	5.5 ⁵³	36.6	101	6.5	9.90	25.1	C _{2v}
1,3	0-25	263.5	0.16 ⁶⁴	0.81 ⁶⁴	6.0 ⁵³	37.5	117	7.1	8.55	23.5	C _{2v}
1,3	—	274	0.28 ⁸	0.79 ⁸	—	—	—	8.3	—	—	C _{2v}
1,4	1-18	278	0.50 ⁶²	0.20 ⁶²	8.0 ⁵³	16	46	16	21.7	8.7	D _{2h}
1,2,3	—	—	—	—	—	—	—	—	—	—	C _{2v}
1,2,4	0	278	0.33 ⁶⁵	0.64 ⁶⁵	—	(19.5) ^c	56	—	17.9	35.9	C _s
1,3,5	0	268	0.035 ⁶⁵	0.45 ⁶⁵	—	—	53	—	1.88	>24.2	D _{3h}
1,2,3,4	0	264.5	0.17 ⁶⁶	0.22 ⁶⁶	—	(35) ^c	(110) ^d	—	—	—	C _{2v}
1,2,3,5	0	268	0.03 ⁶⁶	0.14 ⁶⁶	—	(35) ^c	(110) ^d	—	—	—	C _{2v}
1,2,4,5	0	267	0.34 ⁶⁶	0.52 ⁶⁶	—	(17) ^c	49	—	20.4	30.9	D _{2h}
1,2,3,4,5	1.4	272	0.04 ⁴⁰	—	1.6 ⁵⁹	40	135	1.77	7.4	—	C _{2v}
1,2,3,4,5	20	270	0.025 ⁶⁷	0.06 ^{67d}	1.6 ⁵⁹	64	—	1.66	—	—	C _{2v}
1,2,3,4,5,6	1	280	0.02 ⁸⁸	0.05 ^{38d}	3.6 ⁵⁹	190	500	3.86	2.0	> 5	D _{6h}

^a Value calculated by method of integration of area under absorption curve (refs. 43, 44).^b Assumed value taken from C_{2v} difluorobenzenes.^c Obtained by multiplying $(\tau_R)_{calc.}$ by average value of $\tau_R/(\tau_R)_{calc.}$ for other fluorobenzenes.^d Value inaccurate due to short-lived triplet state.

TABLE 6

RATE PARAMETERS FOR PHOTOPROCESSES IN TRIFLUOROMETHYL (CF₃) BENZENES, VAPOUR PHASE

Position of substituent	Pressure (torr)	Exciting wavelength (nm)	Φ_f	Φ_{isc}	Decay time τ (ns)	τ_R (ns)	τ_R (calc.) ^a (ns)	k_R 10 ⁶ (s ⁻¹)	k_{NR} 10 ⁶ (s ⁻¹)	k_{isc} 10 ⁶ (s ⁻¹)	Point group
0	20	254	0.18 ²⁰	0.72 ⁵⁵	77 ⁴⁵	428	407	2.33	10.6	9.3	D _{6h}
1	10	265	0.16 ²⁹	0.73 ³⁹	19 ⁶³	118	198	8.5	44.5	38.7	C _{2v}
1,3	10	265	0.14 ³¹	0.83 ³¹	18 ⁶⁹	120	239	7.8	47.9	46	C _{2v}
1,4	10	265	0.16 ³²	0.90 ³²	10.7 ⁶⁸	67	100	14.9	78.2	84	D _{2h}

^a Value obtained from method of integration of area under absorption curve.

TABLE 7

RATE PARAMETERS FOR PHOTOPROCESSES IN BENZENES WITH MIXED SUBSTITUENTS, VAPOUR PHASE

Substituents	Positions of substituents	Pressure (torr)	Exciting wavelength (nm)	Φ_f	Φ_{isc}	Decay time, τ (ns)	τ_R (ns)	(τ_R) calc. ^a (ns)	k_R 10 ⁶ (s ⁻¹)	k_{NR} 10 ⁶ (s ⁻¹)	k_{isc} 10 ⁶ (s ⁻¹)
CH ₃ ,F	1,2	4	265	0.225 ³³	0.66 ³³	12 ⁶⁸	52.1	110	19.2	64	56
CH ₃ ,F	1,3	4	265	0.21 ³³	0.75 ³³	13.2 ⁶⁸	65.8	130	15.2	61	57
CH ₃ ,F	1,4	4	265	0.35 ³³	0.62 ³³	13.9 ⁶⁸	39.7	80	25.2	47	45
CF ₃ ,F	1,2	2-13	265	0.225 ¹⁷	—	8.4 ⁶⁸	28.0	70	35.7	83	—
CF ₃ ,F	1,3	3-12	265	0.22 ¹⁷	—	8.6 ⁶⁸	30.7	64	32.6	84	—

^a Value calculated by method of integration of area under absorption curve.

to occur with high probability²⁶, the effects of this process must be considered. If the quenching of the excited singlet state of the aromatic molecule by biacetyl leads to a state of the biacetyl which does not ultimately give rise to phosphorescence, then expression (I) must be modified to:

$$(\Phi_s)_{\text{lim}} \times (\Phi_o/\Phi_f) = \Phi_{\text{isc}} \cdot k_3/(k_3 + k_4) \quad (\text{II})$$

where Φ_o and Φ_f are the quantum yields of fluorescence in the absence of biacetyl, and at the pressure of biacetyl at which $(\Phi_s)_{\text{lim}}$ is measured respectively. Most of the data in Tables 4–7 were obtained by this method, or some variation of it. However, the results of plotting the quantum yield of sensitized emission from biacetyl Φ_s against pressure of biacetyl is a curve which passes through a maximum (e.g. Fig. 1). Some authors have used the maximum value of $(\Phi_s)_{\text{max}}$ obtained in this way^{29–33}, and corrected this value for singlet quenching as above. That this may lead to errors is shown by the result in Fig. 1³³, where it can be seen that the asymptotic value of $(\Phi_s)_{\text{lim}}$ is not reached in the corrected curve until higher pressures of additive than required to give $(\Phi_s)_{\text{max}}$. However, if only small pressures of biacetyl are required for complete triplet quenching, the errors introduced by this procedure will be small. It has been further pointed out that in some cases a fraction of the biacetyl molecules produced by singlet quenching of the aromatic ultimately produce the phosphorescent triplet state³⁴, and thus Φ_s values must be

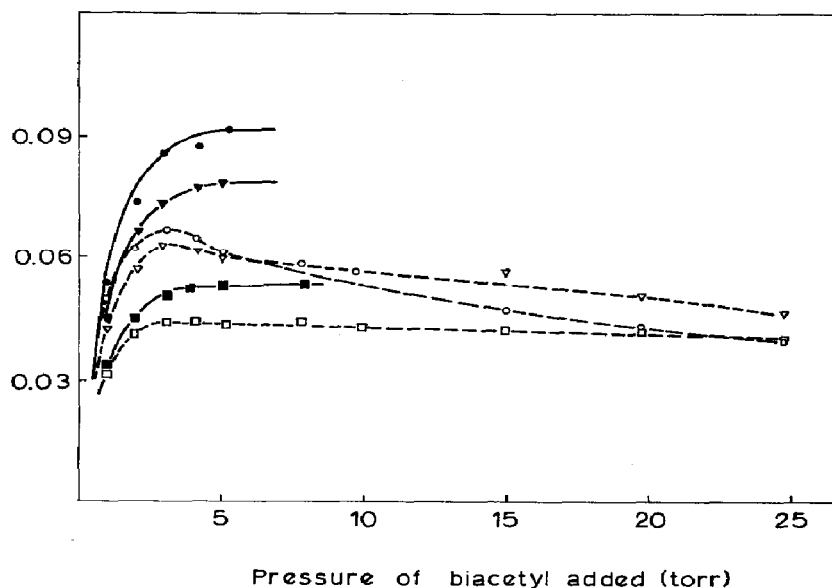


Fig. 1. Quantum yield of phosphorescence of biacetyl sensitized by 1-fluoro-2-methylbenzene excited at various wavelengths as function of pressure of added biacetyl: ---○---○---, 2653 Å, uncorrected for singlet quenching; —●—●—, 2653 Å, corrected results; ---▽---▽---, 2537 Å, uncorrected for singlet quenching; —▼—▼—, 2537 Å, corrected results; ---□---□---, 2482 Å, uncorrected for singlet quenching; —■—■—, 2482 Å, corrected.

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corrected for this. Generally such a procedure has not been carried out, and thus the values quoted in Tables 4-7 for the intersystem crossing quantum yields obtained by the method are accurate only to about 10%, although some results are better in this respect than others.

The alternative method of evaluating Φ_{isc} is dependent upon the measurement of *cis-trans* isomerization of but-2-ene sensitized by the triplet state of the aromatic. Singlet quenching may again be important, but can easily be corrected for by a procedure similar to that outlined above. With this method it is necessary to assume that the triplet state of the olefin decays to the *cis* or *trans* geometrical isomers with an efficiency independent of whether or not the *cis* or *trans* isomer was initially excited in the energy transfer. Thus:



where O is the but-2-ene. It is necessary to know the value of k_6/k_7 in order to evaluate Φ_{isc} , and with the assumed mechanism this can be done by carrying out irradiations under identical conditions with each isomer as starting material in turn. For most aromatic molecules as donors, k_6/k_7 for the but-2-ene was found to be unity^{35,36}, but some donors have been found to sensitize a preferred *cis* to *trans* isomerization in the olefin³⁶. If the basis of the mechanism assumed here is correct, the results obtained are probably accurate to within 5%.

A fuller discussion of the validity of the methods used has been given elsewhere³⁷, and the reader is recommended to this source. Both triplet quenching methods require that experimental conditions be attainable such that the non-radiative decay of the triplet state of the aromatic is entirely suppressed. For molecules with very short triplet lifetimes it is not possible to attain this condition³⁸⁻⁴², and thus true Φ_{isc} values are not available. Finally, the Φ_{isc} values quoted in Tables 4-7 are those which are obtained under conditions which most closely approximate excitation of the aromatic to the zeroth vibrational level of the singlet state.

FLUORESCENCE DECAY TIMES

A discussion of substituent effects must clearly be concerned with comparison of radiative and non-radiative rate constants or lifetimes rather than quantum yields, and it is thus essential to determine absolute values of the rate constants. Until fairly recently the only absolute value of a rate constant available was that for the fluorescence process, [$k_f = 1/(\tau_o)_{calc}$] which was obtained by calculation using the method of integration of area under absorption spectra^{3, 3a, 43, 44}. More recently, however, fluorescence decay time measurements have become standard, using either pulse-sampling techniques^{45, 46} and the more sophisticated photon-

counting pulse fluorometry^{49,50} or modulation methods^{49,50}. Tables 4-6 give values for fluorescence decay times measured under conditions approximating those for which fluorescence quantum yields were measured in the vapour phase. For comparison, values of the radiative lifetime τ_0 obtained experimentally ($\tau_0 = \tau / \Phi_F$) and by the method of integration of areas under absorption curves $(\tau_0)_{\text{calc}}$ are also given in Tables 4-7.

It is evident from Table 4 that the radiative lifetime in the methyl benzenes varies considerably from compound to compound, and moreover correlates well with values expected on the basis of perturbations of orbital symmetry due to the presence of the substituent group^{51,52}. Significantly, the total non-radiative rate constant, or lifetime, does not vary from compound to compound for this series⁵³. These results may be compared with those obtained in the liquid phase, Table 8⁵⁴, from which it can be seen that the alternative non-radiative decay channel, (termed Channel III) is of much greater importance in solution⁵⁴.

For the fluorine-substituted benzenes, fluorescence decay times are not generally available, and whereas for the methyl benzenes there is good agreement between measured and calculated radiative lifetimes, inspection of Tables 5 and 7 reveal that in the case of fluorine substitution the calculated lifetimes are too long by a factor of two to three. It can be seen from Table 5 that using calculated radiative lifetimes, a similar correlation between magnitude of rate constant for fluorescence and symmetry properties exists, but that when true radiative lifetimes are used, such a correlation becomes less marked. Moreover, the magnitude of the non-radiative rate constant varies markedly from compound to compound in this series. This is not unexpected since the magnitude of the rates of non-radiative

TABLE 8

RATE PARAMETERS FOR PHOTOPROCESSES IN METHYL (CH₃) SUBSTITUTED BENZENES, CYCLO
HEXANE SOLUTION

From Table I, A. Reiser and L. Leyshon, *J. Chem. Phys.*, 56 (1972) 1011

Position of substituent	Φ_f	$k_R \times 10^6$ (s ⁻¹)	$k_{NR} \times 10^6$ (s ⁻¹)	Point group
0	0.06	2.0 ± 0.2	33 ± 3	D _{6h}
1	0.14	4.2 ± 0.3	27 ± 3	C _{2v}
1, 2	0.16	4.9 ± 0.3	26 ± 3	C _{2v}
1, 3	0.14	4.8 ± 0.3	30 ± 3	C _{2v}
1, 4	0.33	11.1 ± 0.5	23 ± 3	D _{2h}
1, 2, 3	0.15	4.2 ± 0.3	24 ± 3	C _{2v}
1, 2, 4	0.34	12.5 ± 0.5	25 ± 3	C _s
1, 3, 5	0.14	3.9 ± 0.3	24 ± 3	D _{3h}
1, 2, 3, 4	0.12	4.8 ± 0.3	35 ± 3	C _{2v}
1, 2, 3, 5	0.16	5.3 ± 0.3	28 ± 3	C _{2v}
1, 2, 4, 5	0.25	10.4 ± 0.5	31 ± 4	D _{2h}
1, 2, 3, 4, 5	0.08	4.6 ± 0.3	53 ± 5	C _{2v}
1, 2, 3, 4, 5, 6	0.015	3.2 ± 0.3	240 ± 30	D _{6h}

processes will be determined by the energy differences between the coupled states and the Franck–Condon overlap for the transitions. It is evident from Table 2 that fluorine substitution perturbs the energy levels of the benzene excited states to a much greater extent than methyl substitution, and additionally, leads to greater changes in the geometry of the excited singlet states as revealed by the large changes in Stokes loss in going from the mono- to say penta- and hexa-substituted derivatives⁴⁶ which will accordingly cause variation in the Franck–Condon overlap for different members of the series.

Table 6 shows that the trifluoromethyl substituent also greatly perturbs the benzene system, and that introduction of a fluorine atom to either methyl or trifluoromethyl benzenes produces large changes in radiative and non-radiative rate constants (Table 7).

EXCITATION TO HIGHER VIBRATIONAL LEVELS

Several authors have investigated the effect upon fluorescence quantum yield and decay time of excitation of benzene vapour to single well-defined vibronic levels of the $^1B_{2u}$ state in the collision-free region^{23, 48}, but the definitive study has recently been published⁴⁷, and the results are shown in Table 9. It is evident that particular combinations of vibrational modes critically determine the magnitude of the radiative and non-radiative transition probabilities, and large variations are possible. Several factors mitigate against such thorough studies being carried out on the substituted benzenes. The perturbation of orbital symmetry upon substitution generally causes the radiative transition from the ground state to the excited singlet state to become more allowed than in the case of benzene and thus the density of vibronic levels accessible by optical absorption can become very high. Thus even for a simply substituted benzene such as fluorobenzene analysis of the vibrational structure in the absorption spectrum is incomplete*, and it is thus impossible to identify with precision vibrational levels. Moreover, as the complexity of the molecule increases, the probability of vibrational redistribution of energy into modes of vibration isoenergetic with the optically pumped level, but which are inaccessible themselves by direct absorption, possibly by a unimolecular process³⁷, becomes very large, leading to further difficulties in such molecules.

It is not therefore possible to compare the results quoted below for substituted benzenes with those obtained for single vibronic level excitation of benzene itself, but the results quoted are those which closest approximate the collision-free zone in each case. Figure 2⁵⁹ indicates that in fluorobenzene as the photon energy is increased the magnitude of the radiative lifetime increases, and that for the non-radiative decay processes decreases, and this is seen to be a general trend for other substituted benzenes by inspection of Table 10.

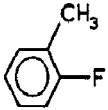
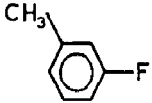
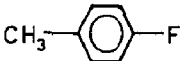
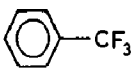
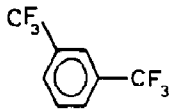
* See however ref. 132.

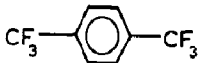
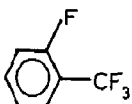
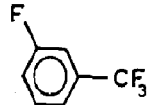
TABLE 9
LIFETIMES AND QUANTUM YIELDS OF SINGLE VIBRONIC STATES IN ${}^1B_{2u}$ BENZENE
(Adapted from Table III, ref. 47)

Vibronic state	% overlap of other states	Energy above origin (cm ⁻¹)	Observer lifetime (ns)	Fluorescence quantum yield	Radiative lifetime, τ_R (ns)	Non-radiative lifetime, τ_{NR} (ns)
0	27	0	100	0.22	455	128
6 ¹	8	521	79	0.27	290	108
6 ¹ 16 ¹	8	764	77	0.26	295	104
1 ¹	28	923	83	0.21	395	105
6 ¹ 16 ³	25	1007	66	0.23	285	86
6 ²	13	1042	72	0.29	250	101
10 ²	52	1170	52	0.16	325	62
6 ² 1 ¹	9	1444	71	0.21	340	90
?	21	1470	65	0.19	340	80
6 ² 11 ²	7	1547	51	0.18	285	62
6 ² 1 ¹ 16 ¹	24	1687	61	0.16	380	73
6 ² 10 ²	43	1691	52	0.24	215	68
1 ²	48	1846	62	0.16	390	74
6 ² 1 ¹ 16 ²	26	1930	49	0.20	245	61
6 ² 1 ¹	9	1965	61	0.22	280	78
6 ² 5 ²	49	2070	55	0.06	920	59
6 ² 1 ²	15	2367	55	0.17	320	66
?	14	2393	39	0.26	150	53
6 ² 1 ² 16 ¹	31	2610	42	0.08	525	46
6 ² 10 ² 1 ¹	18	2614	42	0.06	700	45
1 ²	31	2769	49	0.07	700	53
6 ² 1 ²	19	2888	47	0.03	1470	48

TABLE 10

EFFECTS OF EXCITATION TO HIGHER VIBRATIONAL LEVELS UPON RATES OF PHOTOPROCESSES

Compound	Exciting wavelength (nm)	Φ_f	Φ_{isc}	τ^a (ns)	τ_R (ns)	τ_{NR} (ns)	τ_{isc} (ns)
	265	0.225 ³³	0.66 ³³	12	52.1	15.6	17.9
	254	0.205 ³³	0.62 ³³	11	53.8	13.9	17.9
	248	0.130 ³³	0.45 ³³	10.7	82.6	12.3	23.8
	265	0.20 ³³	0.75 ³³	13.2	65.8	16.4	17.5
	254	0.18 ³³	0.72 ³³	11.7	64.9	14.3	16.4
	248	0.10 ³³	0.40 ³³	12.0	120.5	13.3	30.3
	265	0.35 ³³	0.62 ³³	13.9	39.7	21.3	22.2
	254	0.23 ³³	0.58 ³³	11.3	49.0	14.7	19.6
	248	0.16 ³³	0.42 ³³	10.1	63.3	12.0	23.8
	265	0.16 ²⁹	0.73 ²⁹	19	118	22.5	26.0
	255	0.08 ²⁹	0.41 ²⁹	19	236	20.5	39.3
	248	0.04 ²⁹	0.14 ²⁹	17.6	435	18.2	12.5
	265	0.15 ³¹	0.83 ³¹	18.1	120	21.3	21.7
	248	0.07 ³¹	0.44 ³¹	17.5	250	18.9	40.0
	254	0.11 ³¹	0.67 ³¹	17.0	154	18.9	25.6

Compound	Exciting wavelength (nm)	Φ_f	Φ_{isc}	τ^a (ns)	τ_R (ns)	τ_{NR} (ns)	τ_{isc} (ns)
	265	0.16 ³²	0.90 ³²	10.7	66.7	12.7	11.9
	254	0.10 ³²	0.63 ³²	10.7	106	11.8	16.9
	248	0.06 ³²	0.35 ³²	12.0	200	12.8	34.5
	265	0.295 ¹⁷	—	8.4	28.0	12.0	—
	254	0.22 ¹⁷	—	7.7	35.0	9.9	—
	248	0.10 ¹⁷	—	8.9	88.5	9.8	—
	265	0.29 ¹⁷	—	8.6	30.7	11.9	—
	248	0.22 ¹⁷	—	8.4	59.9	9.7	—
	254	0.30 ¹⁷	—	9.2	30.6	13.2	—

^a Lifetime data from ref. 68.

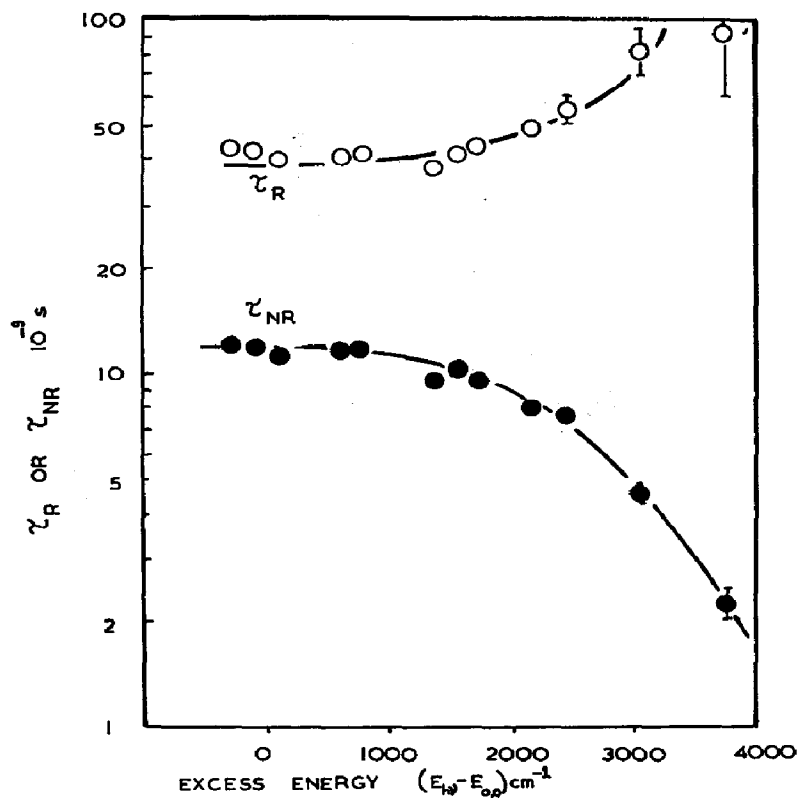


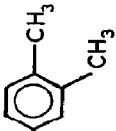
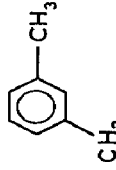
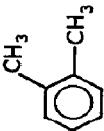
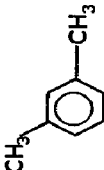
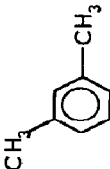
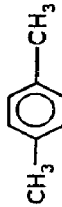
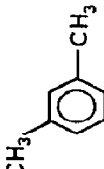
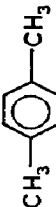
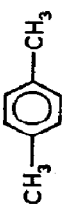
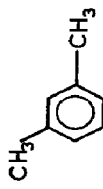
Fig. 2. Radiative and non-radiative lifetimes of fluorobenzene vapour as a function of excess energy above zero point energy of excited 1B_1 state. Based upon Fig. 1, ref. 59.

NATURE OF THE NON-RADIATIVE DECAY PROCESS

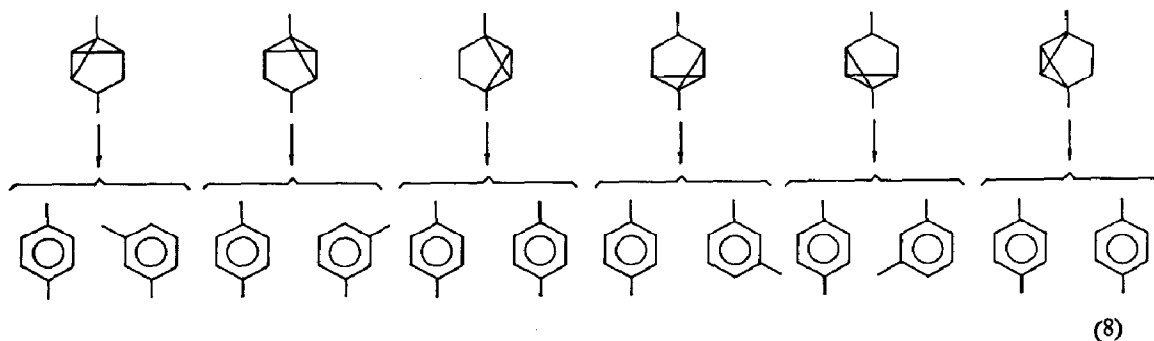
It can be seen that for the vibrationless excited electronic singlet state of most substituted benzenes the non-radiative decay process is principally an intersystem crossing to the triplet manifold. However, it is clear from results in Table 10, and from other quantum yield data on the methyl and fluoro-benzenes that with increase in photon energy, as for benzene, an additional decay channel, termed Channel III becomes of importance. It was speculatively suggested that this decay channel might be associated with isomerization to valence isomers of benzene⁷², of which "benzvalene" is the compound most probably coupled to the ${}^1B_{2u}$ state of benzene^{73, 74}.

The observed 1,2 shifts in the position of substituent in disubstituted benzenes may be related to the formation of "benzvalene" type of intermediate in the following way. The possible isomers formed, and their products assuming equal facility of bond breaking upon rearomatization is illustrated for the 1,4-isomer:

TABLE 11
 QUANTUM YIELDS OF PHOTOISOMERIZATION OF SUBSTITUTED BENZENES, VAPOUR PHASE 25°C

Starting material	Product	Exciting wavelength (nm)	Pressure (torr)	Φ_I	Φ_{BV}	Φ_{NR}	Ref.
		240	1	0.019	0.057	0.985	37
		248	1	0.025	0.075	0.87	37
		240	1	0.039	0.117	0.99	37
		248	1	0.033	0.099	0.96	37
		240	1	0.001	0.003	0.94	37

		248	1	0.002	0.006	0.78	37
		248	2	0.023	0.07	0.94	32
		254	2	0.016	0.05	0.90	32
		248	14.28	0.023	0.07	—	69
		229	∞	0.08	—	—	70
		254	see ref. 71	2×10^{-3}	—	0.93	71



Thus assuming that all benzvalene isomers are formed with equal facility, the quantum yield of formation of the 1,3-isomer can be assumed to represent one-third of the quantum yield of benzvalene formation. Similar reasoning applies to the 1,2- and 1,3-isomers. Quantum yields shown in Table 11 have been calculated in this way. For more heavily substituted fluorobenzenes, it appears that the "Dewar" isomeric product may arise directly from the excited singlet state^{70,71}, in contradiction with the orbital symmetry relationships if the excited states of the substituted molecules are related to those of benzene⁷³. It can be seen from Table 11 that quantum yields of intermediate formation are much too small to account for the magnitude of the Channel III decay process, which suggests that such direct formation of isomers is an insignificant route to the ground state (Table 11). Moreover, it has been pointed out that the principal axes of rotation of benzvalene and benzene lie in different directions⁴⁷, and thus the law of conservation of angular momentum will inhibit conversion of one to the other when the angular momentum of either species is large. The rotational structure of the absorption bands in benzene indicates that there are regions of high, mixed and low angular momentum, and thus excitation of a population of states with large angular momentum should show less benzvalene formation and a correspondingly larger fluorescence quantum yield. The envelopes of the 6_1^0 , 6_0^1 , 6_0^{11} , and $6_0^{11}0^2$ vibronic levels of benzene have been scanned across their rotational substructure recently⁷⁵, and no significant change in the value of the radiative and non-radiative rate constants noted. Although it has been stressed that because of overlap of the P, Q, and R branches complete separation of rotational states cannot be achieved and thus precise separation of regions of high and low angular momentum cannot be scanned, the result supports the notion that direct coupling to an isomeric state cannot occur.

The occurrence of photochemical valence isomerization in the collision-free region has never been probed, of course, and the fact that such a process does occur at higher pressures is not inconsistent with the observations above, in that collisions would remove the angular momentum conservation restriction. Since, however, the quantum yields of formation of valence isomers as revealed by 1,2-shifts in substituted benzenes cannot begin to account for the total value of the

non-radiative decay process, it is tempting to ascribe this to an internal conversion, recognizing that the formation of an unstable intermediate diradical (pre-fulvene)^{73, 79} might nevertheless have a finite existence and play some role in the decay process*.

VIBRATIONAL RELAXATION AND REDISTRIBUTION

As has been stated earlier, the technique of excitation of single vibronic levels in benzene vapour has been used to demonstrate that the zeroth vibrational level of the ${}^1B_{2u}$ state emits to comparatively few vibrational levels, giving a simple fluorescence spectrum²³, whereas that for benzene vapour excited to higher vibrational levels and subsequently collisionally relaxed to the Boltzmann distribution is very complex, consisting of many bands with an underlying continuum of levels, as seen in Fig. 3²³. It has been shown that the collision cross-section for the relaxa-

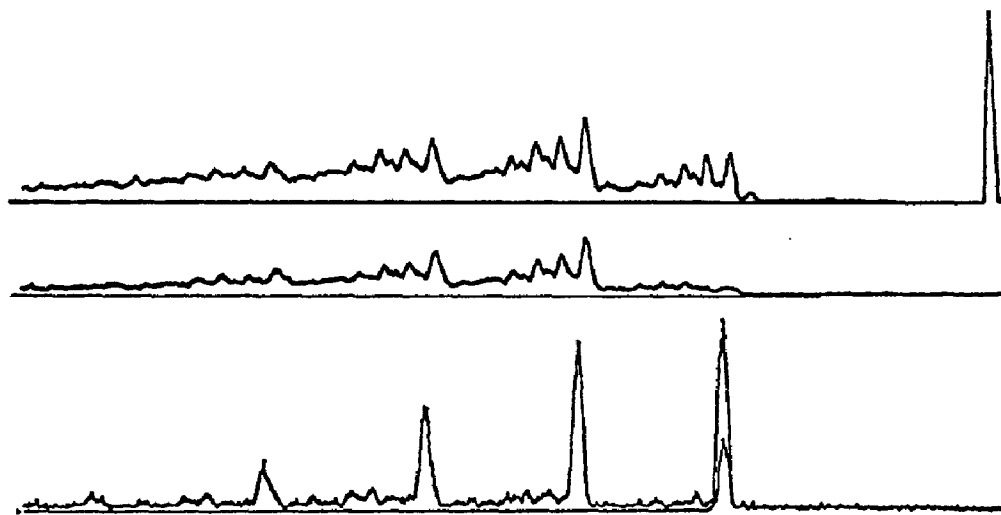


Fig. 3. A comparison of the spectrum of fluorescence from the zero-point level with those from a 300 K Boltzmann distribution of vibrational levels in the ${}^1B_{2u}$ state of benzene- h_6 vapour. The bottom spectrum is from the zero-point vibrational level. The upper spectra are each from a Boltzmann distribution of vibrational levels obtained by addition of isopentane at a heat bath. The top spectrum is from 0.1 Torr of C_6H_6 in the presence of 100 Torr of isopentane using the 2537 Å Hg line to excite the upper state of benzene. The intense band at the far right is Rayleigh scattered 2537 Å radiation. The features in the spectrum have been assigned by F. M. Garforth and C. K. Ingold, *J. Chem. Soc.*, (1948) 427. The centre spectrum is obtained from 8 Torr of benzene with 92 Torr of added isopentane and is excited with radiation identical to that used for the bottom spectrum. The centre spectrum closely matches the top spectrum with the exception of the first group of bands on the right. Reabsorption of fluorescence by benzene at high pressure distorts these bands from their true intensities.

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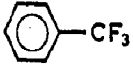
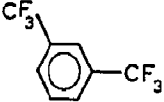
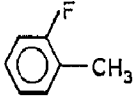
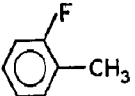
* See notes added in proof on page 146.

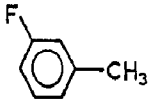
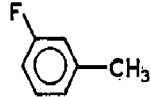
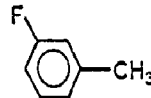
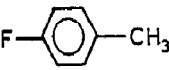
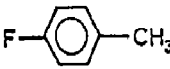
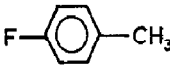
tion/redistribution process is very large, being greater by a factor of five than the gas kinetic hard sphere collision cross-section²³. No comparable data for the substituted benzenes exist, but in toluene and the xylenes it was found necessary to suppose that the redistribution of vibrational energy to the dense manifold of levels not coupled to the ground state was also extremely efficient, both unimolecular and collisional contributions being of importance³⁷.

For some compounds [e.g. the xylenes³⁷, (trifluoromethyl) benzene²⁹], excitation of the molecule by absorption of light close to the long-wavelength cut-off of the absorption spectrum produces a set of vibronic states, the average quantum yield of fluorescence of which is such that collisional relaxation/redistribution causes decrease in the fluorescence quantum yield. For most molecules, however, excitation under these conditions produces a set of levels from which collisional relaxation or redistribution produces levels with an average quantum yield of fluorescence insignificantly different from the initial set, so that no observed change occurs^{53, 56}. In most molecules, excitation to higher vibrational levels generally produces states with an average fluorescence quantum yield less than that of the relaxed molecule, and collisions thus cause an overall increase in the fluorescence quantum yield⁷⁶. In all cases where collision causes change in quantum yield, an approximate idea of the efficiency of the collisional processes may be obtained from kinetic analysis of the data. For benzene itself excited at 253.7 nm, several authors have proposed a two-step mechanism for vibrational relaxation^{46, 49, 77, 78}. The two level mechanism has been criticized, and a three-level mechanism suggested⁷⁹, for which quantum yield data are said to fit the scheme more exactly. The problem of analysis of data in terms of a multi-step cascade mechanism for vibrational relaxation/redistribution has been discussed by many authors⁸⁰⁻⁸⁶. Generally, if n vibronic levels are considered, expressions relating quantum yields to pressure contain n th degree polynomials, and analysis is complex. A very simple approach has been proposed⁸⁷ on which it has been shown that for a one-step relaxation, plots of $(\Phi_f - \Phi_u)/(\Phi_o - \Phi_f)$ where Φ_n , Φ_f and Φ_o are the values of the average quantum yield of fluorescence in the collision free zone, at any pressure of additive [M] and at infinite pressure of additive respectively against concentration [M] should be straight lines from which the average rate constant and cross-section for the relaxation can be obtained. A more complex multi-step cascade leads inevitably to a more complex relationship, but using the crude approximation that only the terms in highest power of concentration of additive are important, an approximate idea of the order of magnitude of the number of steps necessary for relaxation, and the cross-section for relaxation can be obtained. A selection of such parameters is shown in Table 12, and it can be seen that generally relaxation is effected most efficiently by the ground state of the aromatic itself, with cross-sections generally approaching the gas kinetic. It should be stressed that the values in Table 12 may have no absolute validity given the simplicity of the models used, but that the values obtained are not inconsistent

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TABLE 12 (continued)

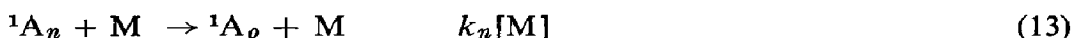
Aromatic	Collision partner	Exciting wavelength (nm)	k_n/k_{1n} (10^2 l mol^{-1})	Ref.	k_n 10^{10} ($\text{l mol}^{-1}\text{s}^{-1}$)	No. collisions	Energy lost per collision	σ^a 10^{-16} (cm^2)
	SF ₆	265	6.4	29	0.9	(1) ^b	4-8	1.6
	N ₂	248	5.4	29	0.8	(1) ^b	4-8	0.8
	cyclo-C ₆ H ₁₂	248	15	29	0.35	(1) ^b	38	0.52
	C ₂ H ₄	248	10.8	29	0.24	(1) ^b	38	0.24
	But-2-ene	248	9.1	29	0.20	(1) ^b	38	0.25
	CF ₃ CF=CFCF ₃	248	6.9	29	0.16	(1) ^b	38	0.28
	cyclo-C ₄ F ₈	248	5.4	29	0.12	(1) ^b	38	0.24
	CH ₂ =CF ₂	248	4.1	29	0.095	(1) ^b	38	0.14
	SF ₆	248	63	31	2.5	(1) ^b	38	5.0
	CF ₃ CF=CFCF ₃	248	54	31	2.16	(1) ^b	38	4.4
	C ₂ H ₄	248	37	31	1.48	(1) ^b	38	1.6
	CH ₂ CF ₂	248	23	31	0.92	(1) ^b	38	1.3
	cyclo-C ₄ F ₈	248	74	31	2.96	(1) ^b	38	6.4
			$k_n \sum k_n$ $10^2 (\text{l mol}^{-1})$					
		248	4.95	87	4.6	1	38	14.4
	cyclo-C ₄ F ₈	248	0.39	87	0.36	1-2	26	0.7
	But-2-ene	248	0.61	87	0.57	1-2	28	0.7

		254	8.34	87	7.1	1-2	19	21
		248	4.82	87	4.0	1-2	30	12
	cyclo-C ₄ F ₈	248	0.38	87	0.32	1	35	0.6
	But-2-ene	248	0.51	87	0.43	1	46	0.5
		254	11.8	87	10.4	3	12	33
		248	8.34	87	8.3	3	16	25
	cyclo-C ₄ F ₈	248	0.56	87	0.55	1	43	1.0
	But-2-ene	248	0.80	87	0.80	1	64	1.0

^a Obtained from the equation $\sigma^a = k_n (8\pi kT/\mu)^{-1/2}$

^b Assumed value of unity.

with the data for the benzene molecule indicates that they may have order of magnitude significance. The model used for relaxation in the trifluoromethyl, and mixed substituent cases produces results for the collisional relaxation processes only, whereas the fuller analysis in the case of the xylenes produces results for the unimolecular process also. The rate constants tabulated in Table 12 relate to the following scheme:



QUENCHING OF EXCITED SINGLET STATES

Aside from vibrational effects upon addition of gases to benzene and substituted benzenes excited near the zero-zero transition, the excited singlet states of the aromatic may be quenched by the additive by four main mechanisms. These are: (a) electronic energy transfer, (b) enhancement of S_1-T_1 intersystem crossing, (c) charge-transfer interaction, and (d) chemical addition.

Clearly (a) is limited to those additives which have states with electronic energies lower than those of the benzenes, if the process is to be at all efficient. (b) is restricted to those molecules containing an atom with high nuclear charge and molecular oxygen. (c) may involve charge-transfer from the aromatic excited state to the additive, or the reverse depending upon the relative ionization potentials and electron affinities of the aromatic molecule and quenching partner, and may precede (d).

Table 13 gives all data available to date on the quenching efficiency of various additives for ${}^1B_{2u}$ benzene. In most cases pressures of benzene have been used such that the Boltzmann distribution of emitting levels is produced prior to interaction with the additive. The rate quenching parameters thus represent averages for this distribution of vibrational levels, but as such are comparable to one another.

It is evident that the ketones at the top of Table 13 are the most efficient quenchers, and compare favourably with other molecules known to have singlet states lower in energy than that of benzene. Mechanism (a) clearly operates in these cases, and effects of steric hindrance upon the efficiency of the energy transfer process have been discussed⁹¹. Molecular oxygen is seen to be extremely

TABLE 13

QUENCHING OF EQUILIBRATED ¹B_{2u} BENZENE

Benzene pressure = 15–20 torr^a

Exciting wavelength 254 nm, ambient temperature

Quencher	Ref.	Rate constant 10 ¹⁰ (l mol ⁻¹ s ⁻¹)	Cross-section 10 ⁻¹⁶ (cm ²)	Quencher	Ref.	Rate constant 10 ¹⁰ (l mol ⁻¹ s ⁻¹)	Cross-section 10 ⁻¹⁶ (cm ²)
CS ₂	88	14.6	18.4	1,5-Hexadiene	92	0.055	0.073
3-Methylpentenal	88	14.6	18.4	Tetramethylethylene	92	0.052	0.069
2-Pentanone	89	14.6	18.4	1,4-Pentadiene	92	0.047 (0.0186) ^b	0.057 (0.023)
4-Pentenal	88	13.9	17.5	Trimethylethylene	92	0.043 (0.015) ^b	0.052 (0.019)
Biacetyl	88	12.35	15.8	But-2-ene	92	0.0345 (0.0075) ^b	0.040 (0.009)
O ₂	88	10.3	9.9	CH ₂ =CF ₂	93	0.025	0.039
O ₂	90	12.6	12.1	Propylene	92	0.0235 (0) ^b	0.026 (0)
3-Pentanone	91	9.77	13.1	CF ₃ -CF=CF-CF ₃	93	0.0235	0.037
Acetone	91	8.27	10.4	CH ₂ =CHF	93	0.0175	0.019
Cyclobutanone	88	8.20	10.1	CCl ₄	94	0.39	0.58
Cyclopentanone	88	8.20	10.5	CH ₃ Br	94	0.17	0.24
Cyclohexanone	88	8.20	11.0	CH ₃ Cl	94	0.046	0.053
2-Butanone	91	8.09	10.4	CH ₂ ClCH ₂ Cl	94	0.031	0.043
2,4-Dimethyl-3-pentanone	91	6.24	8.92	CHCl ₃	94	0.024	0.034
2,2,4,4-Tetramethyl-1,3-pentanone	91	2.03	3.02	CHF ₃	94	0.024	0.030
cis-1,3-pentadiene	88	1.49	1.84	CH ₂ Cl ₂	94	0.024	0.032
cis-1,3-pentadiene	92	1.40 (1.36) ^b	1.73 (1.68)	Xc	95	0.020	0.029
trans-1,3-pentadiene	88	1.37	1.67	CF ₄	94	0	0
Isoprene	92	0.95 (0.92) ^b	1.16	Propane	92	0.025 (0) ^b	0
1,3-Butadiene	88	0.57	0.66	2,3-Dimethylbutane	92	0.031 (0) ^b	0
1,3-Butadiene	92	0.56 (0.52) ^b	0.63 (0.59)	Cyclohexane	92	0.028 (0) ^b	0
1,3-Butadiene-d ₄	88	0.50	0.59	CH ₃ NH ₂	106	1.94	1.92
COS	88	0.44	0.48				
cis-ClHC=CHCl	93	1.04	0.14				
trans-ClHC=CHCl	93	0.076	0.105				
CH ₂ =C=CH ₂	93	0.077	0.083				
1,2-Butadiene	92	0.061	0.069				

^a In ref. 88, 2.5 torr benzene was used.

^c Cross-sections quoted from equation $\sigma^2 = k_0(8\pi kT/\mu)^{-1/2}$.

^b The total rate constant is assumed to contain contributions from vibrational relaxation. The value in parentheses is believed to be that for electronic quenching alone.

efficient in quenching the excited $^1B_{2u}$ state of benzene, by a mechanism which leads to $^3B_{1u}$ formation⁹⁰. Xenon is also effective in this respect⁹⁵, but halogenated compounds are generally too efficient to be considered to act in this way⁹⁴. It is likely that halogenated compounds quench by a charge-transfer mechanism in which the benzene $^1B_{2u}$ acts as an electron donor, and such complex formation may be followed by chemical breakdown in the halogenated compound⁹⁶⁻⁹⁸. Olefins are seen to be relatively inefficient quenchers of $^1B_{2u}$ benzene, and it has been proposed that charge-transfer is again responsible^{92, 93}, but in the opposite sense. Thus a rough correlation between quenching efficiency and ionization potential of the olefin is observed, as shown in Fig. 4⁹³, which is as expected for this process. It can be seen, however, that the efficiency of mono-olefins is approximately equal to that of hydrocarbons in quenching the benzene fluorescence, which is attributable to vibrational relaxation, not electronic quenching⁹². Although such

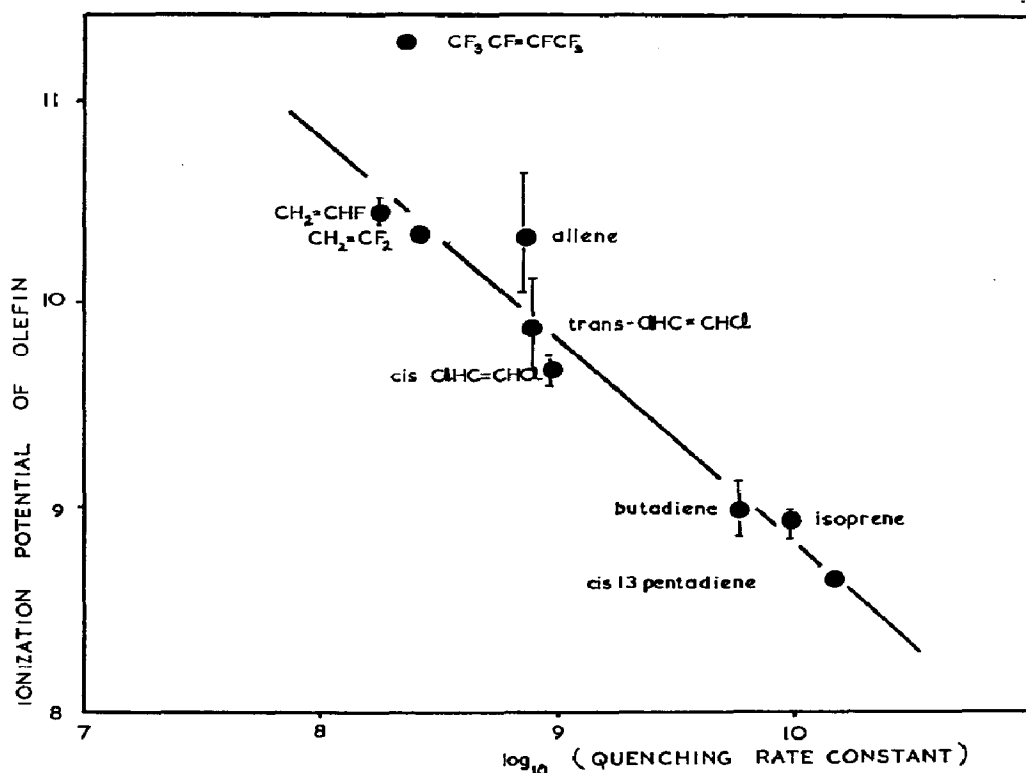

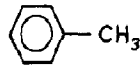
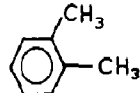
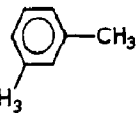

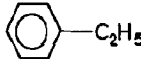
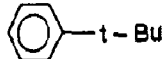
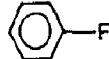
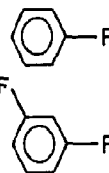


Fig. 4. Plot of \log (quenching rate constant) against ionization potential for a selection of olefins and $^1B_{2u}$ benzene. It should be stressed that the data have been selected from Table 13 to illustrate the *possible* involvement of charge-transfer interaction. However, there are many olefins (and other compounds) for which the apparent quenching rate constant is of the order of 10^8 (see Table 13). There is no correlation between the efficiency of these molecules in quenching and their ionization potentials. It is likely that the apparent quenching observed in such cases may be due to enhancement of the collisional redistribution of vibrational energy, so that the alternative decay process (channel III) becomes of increasing importance. This must be the case since Φ_f for benzene in solution is only 0.06.

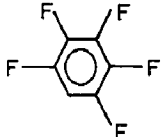
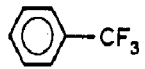
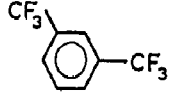
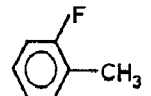
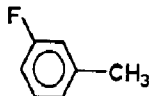
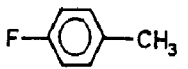

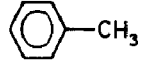
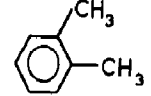
TABLE 14

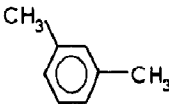
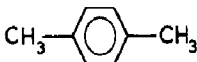
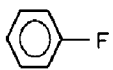
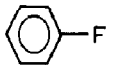
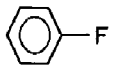
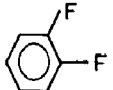
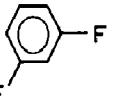
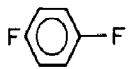
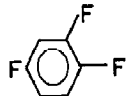
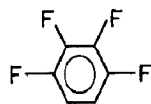
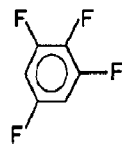
QUENCHING OF EXCITED SINGLET STATES OF SUBSTITUTED BENZENES

Aromatic	Quencher	Exciting wavelength (nm)	Quenching rate constant 10^{10} ($1 \text{ mol}^{-1}\text{s}^{-1}$)	Quenching cross-section ^a 10^{-16} (cm^2)	Ref.	Relative rate constants
	O_2	254	10.3	9.9	88	(1.00)
	O_2	254	23.4	23.9	88	2.27
	O_2	267	19.3	19.7	56	1.87
	O_2	271	12.65	13	37	1.23
	O_2	248	35.5	37	37	3.45
	O_2	272.5	9.64	9	37	0.94
	O_2	253	18.07	19	37	1.75
	O_2	274	11.4	12	37	1.11
	O_2	248	29.5	31	37	2.86
	O_2	264	22.3	22.3	104	2.17
	O_2	264	25.3	27.1	104	2.46
	O_2	265	22.4	23.1	30	2.17
	O_2	265	20.6 ^b	21.2	58	2.00
	O_2	271	24.0 ^b	25.2	104	2.33

(continued)

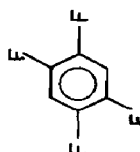
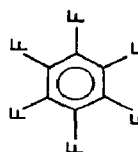
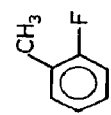
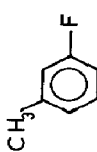
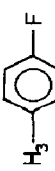

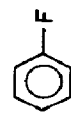
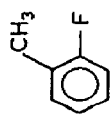
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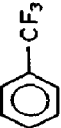
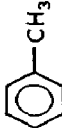

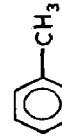
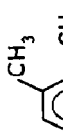
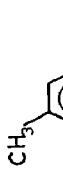
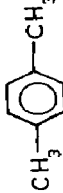
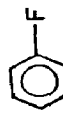
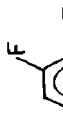
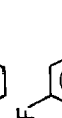
Aromatic	Quencher	Exciting wavelength (nm)	Quenching rate constant 10^{10} ($l \text{ mol}^{-1} \text{ s}^{-1}$)	Quenching cross-section ^a 10^{-18} (cm^2)	Ref.	Relative rate constants
	O ₂	265	2.08 ^b	2.26	40	0.20
	O ₂	265	10.22 ^c	11.0	29	0.99
	O ₂	265	7.2 ^c	8.1	30	0.70
	O ₂	265	17.5	17.5	87	1.70
	O ₂	265	14.0	14.0	87	1.37
	O ₂	265	27.1	27.1	87	2.63
	Biacetyl	254	12.35	15.8	88	(1.00)
	Biacetyl	266	24.9	31.2	131	2.02
	Biacetyl	271	33.4	51	37	2.70

	Biacetyl	271	27.2	45	37	2.20
	Biacetyl	271	33.0	53.5	37	2.67
	Biacetyl	265	21.5 ^b	27.4	34,58	1.74
	Biacetyl	265	25 ^d	31.9	30	2.02
	Biacetyl	267	19.4 ^b	24.7	61	1.57
	Biacetyl	270	12.6 ^b	16.4	62	1.02
	Biacetyl	262	10.9 ^b	14.2	8	0.88
	Biacetyl	274	19.5 ^b	25.4	62	1.58
	Biacetyl	278	16.5 ^b	22.0	65	1.34
	Biacetyl	265	4.05 ^{b,e}	5.5	66	0.33
	Biacetyl	268	18.2 ^b	24.8	66	1.47

(continued)

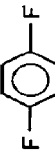

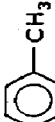
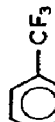

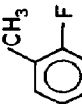
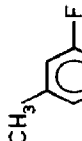

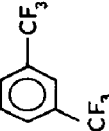
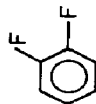
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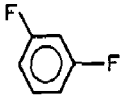
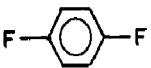

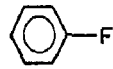
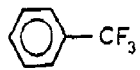
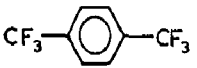
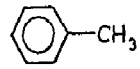
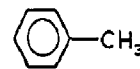
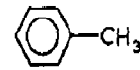
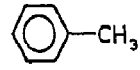
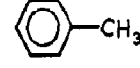
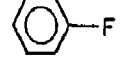
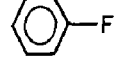
Aromatic	Quencher	Exciting wavelength (nm)	Quenching rate constant 10^{10} ($l \text{ mol}^{-1} \text{ s}^{-1}$)	Quenching cross-section ^a 10^{-16} (cm^2)	Ref.	Relative rate constants
	Biacetyl	267	57.5 ^b	78.3	66	4.66
	Biacetyl	265	22 ^b	30.8	38	1.78
	Biacetyl	265	29.5	43	87	2.89
	Biacetyl	265	30.1	43.7	87	2.44
	Biacetyl	265	26.1	37.8	87	2.11
	2-Pentanone	254	14.6	18.4	89	(1.00)
	2-Pentanone	265	24.1	34.2	30	1.65
	2-Pentanone	265	20.5	30.9	105	1.40

	2-Pentanone	265	26.3	39.6	105	1.80
	2-Pentanone	265	39.6	64.1	105	2.71
	2-Pentanone	265	19.5	28.1	105	1.34
	Cyclopentanone	254	15.7	21	63	(1.00)
	Cyclopentanone	264	17.8	24.8	63	1.13
	Cyclopentanone	270	19.71	28.4	63	1.26
	Cyclopentanone	271	17.49	25.2	63	1.11
	Cyclopentanone	272	24.29	35	63	1.55
	Cyclopentanone	265	23.0	31	63	1.46
	Cyclopentanone	266	26.6	39	63	1.69
	Cyclopentanone	265	25.3	37	63	1.61

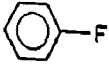
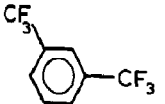
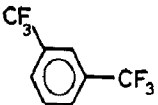
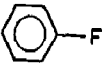
(continued)

Table 14 (continued)

Aromatic	Quencher	Exciting wavelength (nm)	Quenching rate constant 10^{10} ($l \text{ mol}^{-1} \text{ s}^{-1}$)	Quenching cross-section ^a 10^{-16} (cm^2)	Ref.	Relative rate constants
	Cyclopentanone	280	34.15	50	63	2.18
	Buta-1,3-diene	254	0.57	0.66	88	(1.00)
	Buta-1,3-diene	254	1.54	1.87	88	2.70
	Buta-1,3-diene	265	5.57	7.4	29	9.77
	Buta-1,3-diene	265	2.23	3.2	30	3.91
	Buta-1,3-diene	265	0.9	1.15	87	1.58
	Buta-1,3-diene	265	1.16	1.50	87	2.04
	Buta-1,3-diene	265	2.98	3.83	87	5.23
	Buta-1,3-diene	265	10.67	14.7	31	18.7
	Buta-1,3-diene	265	2.68 ^b	3.4	105	4.70

	Buta-1,3-diene	265	2.97 ^b	3.75	105	5.21
	Buta-1,3-diene	265	3.6 ^b	4.6	105	6.32
	But-2-ene	254	0.035 (0.008)	0.040 (0.009)	92	(1.00)
	But-2-ene	265	0.066	0.085	30	1.89
	But-2-ene	265	0.93	1.22	29	26.6
	But-2-ene	265	2.82	3.65	31	80.57
	CS ₂	254	55	74.6	88	—
	Cyclobutanone	254	33	44.0	88	—
	Cyclohexanone	254	32.5	47.2	88	—
	<i>cis</i> -1,3-Pentadiene	254	3.25	4.2	88	—
	1,3-Butadiene-d ₆	254	1.32	1.64	88	—
	Perfluoro-but-2-ene	265	0.174	0.30	30	—
	CH ₂ =CF ₂	265	0.018	0.03	30	—

(continued)

Aromatic	Quencher	Exciting wavelength (nm)	Quenching rate constant $10^{10} (1 \text{ mol}^{-1} \text{ s}^{-1})$	Quenching cross-section ^a $10^{-16} (\text{cm}^2)$	Ref.	Relative rate constants
	$\text{CH}_2=\text{CH}_2$	265	0.054	0.05	30	—
	Perfluoro-but-2-ene	265	0.16 ^c	0.19	31	—
	$\text{CH}_2=\text{CF}_2$	265	0.11 ^c	0.11	31	—
	Xe	265	9.1	14.3	107	—

^a Given by the equation $\sigma^2 = k_a(8\pi kT/\mu)^{-1/2}$

^b Values from the reference given normalized to the radiative rate constant given in Table 5.

^c Values from the reference given normalized to radiative rate constant given in Table 6.

^d The value quoted in Table 1, ref. 30 is in error. The correct value shown here was obtained from Fig. 3, ref. 30.

^e This value appears to be too small, possibly, due to incorrect assumption of radiative lifetime.

vibrational effects were apparently absent in the study using a pressure of 20 torr benzene⁹³, (result for CF₄), they cannot be ruled out definitely however, and thus the mono-olefin results must be treated with caution. Cyclo-addition of olefins to benzene is known to occur⁹⁹⁻¹⁰³, although in small yield, and it is possible that charge transfer interaction is followed by such reactions. However, some of the addition products may arise from addition to an intermediate of the "prefulvene" type, in which case the quenching of fluorescence would be unrelated to the product formation.

The quenching of the excited singlet states of other aromatic donors by various additives is shown in Table 14. It is evident that presence of a substituent in the benzene ring can give rise to extraordinarily efficient electronic energy transfer to acceptor molecules such as ketones, and moreover charge-transfer interactions may also be enhanced. The very high cross-section for the energy transfer processes in these cases lead to speculation that a long-range dipole-dipole Forster type interaction might play some part in the overall process^{53, 63}. The quenching of the trifluoromethyl benzenes by olefins is clearly much more efficient than for corresponding methyl or fluorine substituted benzenes.

QUENCHING OF EXCITED TRIPLET STATES

In principle, the ³B_{1u} state of benzene may be quenched by any of the mechanisms above, replacing (b) by the T₁ → S₀ non-radiative transition. In practice, however, quenching by most additives appears to be predominantly by an electronic energy transfer process. The use of such processes to monitor S₁ → T₁ intersystem crossing quantum yields has already been commented upon. Flash photolysis studies on 20 torr benzene and added biacetyl have allowed estimation for the lifetime of the triplet state of benzene under these conditions as $2.6 \pm 0.5 \times 10^{-5} \text{ s}^{108}$, and the rate constant for energy transfer from triplet benzene to biacetyl as $3.42 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}^{108}$. These values have allowed confirmation of the quantum yield of intersystem crossing in biacetyl vapour¹⁰⁹.

From quenching experiments in which biacetyl and but-2-ene are in competition for the triplet state of benzene, the rate constant for the energy transfer process to the olefin may be estimated as $9 \pm 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (Table 15)¹¹⁰. A recent study in which the rate constant for the latter process was measured directly using a modulation technique yields a result which is in good agreement, $8.95 \pm 0.33 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}^{111}$. However, such agreement may well prove to be fortuitous since it has been demonstrated that under the conditions of the modulation experiment the decay of the ³B_{1u} benzene is accounted for almost entirely by second-order interaction^{112, 113}, with a residual first-order decay which could be accounted for entirely by quenching by impurities such as molecular oxygen present in low concentration. In contrast, the flash photolysis experiments indicated that no second-order effects were important, and thus the decay rate constant

TABLE 15

QUENCHING OF $^3\text{B}_{1u}$ BENZENE IN VAPOUR PHASE

Quencher	Benzene pressure	Competitor ^a and pressure	k_B/k_Q^b	k_Q/k_C^c	$k_Q^d 10^8$ ($1 \text{ mol}^{-1}\text{s}^{-1}$)	$\sigma^2 10^{-18}$ (cm^2)	Ref.
Biacetyl	20	—	(1.00)	—	34.3	4.39	108
<i>cis</i> -But-2-ene		—	—	(1.00)	8.95 ± 0.33	1.02	111
<i>cis</i> -But-2-ene	2.5	B,0.31	3.85	(1.00)	8.91	1.01	110
1,3-Butadiene	2.5	B,0.31	0.183	21	187.2	21.7	110
1,3-Butadiene	2.5	C,1	0.32, 0.28	12, 14	106.9, 124.7	12.4, 14.5	114, 116
1,3-Butadiene	10–15	C,10–15	0.238	16.2	131.1	15.2	115
<i>trans</i> -1,3-Pentadiene	2.5	C,2.5	0.241	16	142.5	18.0	116
<i>cis</i> -1,3-Pentadiene	2.5	C,2.5	0.226	17	151.5	19.2	118
CS ₂	2.5	C,2.5	0.128	30	267.3	34.9	116
1,3-Butadiene	2.5	C,2.5	0.275	14	124.7	14.8	116
1,5-Pentadiene	2.5	C,2.5	3.85	1.0	8.91	1.13	116
4-Pentenal	2.5	B,0.31	1.07	3.6	32.1	4.29	110
4-Pentenal	2.5	C,1	1.28	~3	26.7	3.57	114
Tetramethylethylene	2.5	B,0.31	1.32	2.92	26.0	3.48	110
Tetramethylethylene	2.5	C,1	1.24	3.1	27.6	3.69	114
Tetramethylethylene	10–15	C,10–15	1.44	2.67	23.8	3.18	115
2-Methylbut-2-ene	2.5	B,0.31	2.05	1.88	16.7	2.13	110
CH ₃ NH ₂	20	B,0.35	1.15	3.35	29.85	2.95	106
2-Methylbut-2-ene	2.5	C,1	2.26	1.7	15.15	1.93	114
2-Methylbut-2-ene	10–15	C,10–15	2.39	1.61	14.34	1.83	115
1,4-Cyclohexadiene	2.5	B,0.31	2.61	1.48	13.19	1.74	110
Cyclohexene	2.5	B,0.31	2.7	1.4	11.33	1.50	110
Cyclopentene	2.5	B,0.31	3.62	1.06	9.44	1.20	110
Cyclopentene	2.5	C,1	4.38	0.88	7.84	1.00	114
<i>trans</i> -But-2-ene	2.5	B,0.31	3.73	1.03	9.18	1.10	110
<i>trans</i> -But-2-ene	2.5	C,1	3.53	1.09	9.71	1.16	114
2-Methylbut-1-ene	10–15	C,10–15	4.81	0.80	7.13	0.91	115
Isobutene	10–15	C,10–15	3.03	1.27	11.3	1.36	115
Pent-1-ene	2.5	B,0.31	8.9	0.43	3.83	0.49	110
Pent-1-ene	2.5	C,1	7.86	0.49	4.37	0.56	114

J. Photochem., 1 (1972/73)	Pent-1-ene	10-15	C,10-15	7.13	0.54	4.81	0.62	115
	But-1-ene	2.5	B,0.31	8.34	0.46	4.09	0.49	110
	But-1-ene	2.5	C,1	7.86	0.49	4.37	0.52	114
	But-1-ene	10-15	C,10-15	7.70	0.50	4.45	0.53	115
	Propylene	2.5	B,0.31	9.1	0.42	3.74	0.41	110
	Propylene	2.5	C,1	6.75	0.53	4.72	0.52	114
	Propylene	10-15	C,10-15	8.19	0.47	4.19	0.46	115
	CH ₃ -CD=CD ₂	2.5	C,2.5	13.28	0.29	2.58	0.29	116
	Propylene-d ₆	2.5	C,2.5	12.03	0.32	2.85	0.33	114
	Allene	2.5	C,1.5	15.4	0.25	2.23	0.24	116
	Allene	20	B,0.35	21.39	0.18	1.60	0.17	93
	Ethylene	2.5	B,0.31	17.8	0.22	1.96	0.19	110
	Ethylene	2.5	C,2.5	16.74	0.23	2.05	0.20	116
	Ethylene	2.5	C,1	20.26	0.19	1.69	0.16	114
	Ethylene	2.5	C,10-15	17.50	0.22	1.96	0.19	115
	CH ₂ =CD ₂	2.5	C,2.5	29.61	0.13	1.16	0.11	116
	CD ₂ =CD ₂	2.5	C,2.5	29.61	0.13	1.16	0.11	116
	CH ₂ =CHF	20	B,0.35	29.61	0.13	1.16	0.13	93
	CH ₂ =CF ₂	20	B,0.35	26.4	0.145	1.3	0.15	93
	<i>cis</i> -CHCl=CHCl	20	B,0.35	490	0.008	0.07	0.01	93
	<i>trans</i> -CCl=CHCl	20	B,0.35	0.53	7.26	65	9.0	93
	CH≡CH	2.5	C,2.5	0.53	7.26	65	9.0	116
	CF ₃ -CF=CF-CF ₃	20	B,0.35	7.70	0.005	0.045	0.0042	93
	CCl ₄	20	B,0.35	2.01	1.89	17	2.7	94
	CHCl ₃	20	B,0.35	∞	0	<0.007	0	94
	CH ₂ Cl ₂	20	B,0.35	1143	0.003	0.03	0.04	94
	H ₂ CICH ₂ Cl	20	B,0.35	1143	0.003	0.03	0.04	94
	CH ₃ Br	20	B,0.35	∞	0	0	0	94
CH ₃ Cl	20	B,0.35	1715	0.002	0.02	0.027	94	
CHF ₃	20	B,0.35	∞	0	<0.007	0	94	
			3430	0.001	0.01	0.01		

^a B = biacetyl; C = *cis*-but-2-ene.

^b k_B = rate constant for quenching by biacetyl k_Q that by additive 94.

^c k_C = rate constant for quenching by *cis*-but-2-ene.

^d Normalized to value for biacetyl of ref. 108.

of $2.6 \pm 0.5 \times 10^{-5} \text{s}^{-1}$ represents a true unimolecular decay rate constant¹⁰⁸, some two orders of magnitude greater than that obtained in the modulation experiment. Since it is unlikely that in the flash experiments some two orders of magnitude greater concentration of impurity was present, reproducible from run to run, it would appear that there is a real discrepancy between the two sets of data. Table 15 gives rate constant data for quenching of $^3\text{B}_{1u}$ benzene based on the value for transfer to biacetyl quoted above.


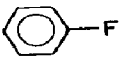
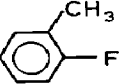
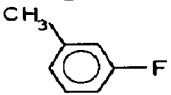
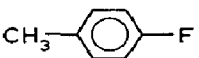
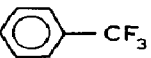
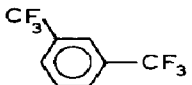

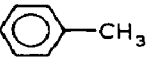
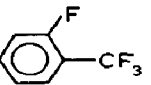
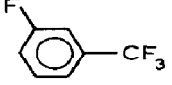

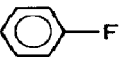
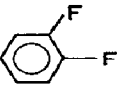
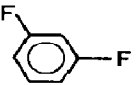

Noteworthy points in Table 15 are that only di-olefins compete more effectively for triplet benzene than biacetyl, although dichloro-ethylenes appear to be very efficient also. The inefficiency of mono-olefins in this respect may be due to near degeneracy of triplet energy levels of the aromatic molecule and quencher. Halogenated compounds probably quench by complex formation, which may precede dissociation of the quencher^{117,118}. One study has indicated that only vibrationally excited triplet benzene may cause such dissociation¹¹⁹.

For substituted benzenes, gas-phase triplet lifetimes are not available, and thus absolute values of rate constants for quenching cannot be evaluated. Competitive quenching experiments using biacetyl as reference have in some cases been carried out, however, and the results are summarized in Table 16. The data in Table 16 may be supplemented by the additional qualitative observations that the triplet states of 1,2-difluorobenzene⁶², 1,3-difluorobenzene⁸ and 1,3,5-trifluorobenzene⁶⁵ are quenched by moderate pressures of *cis*-but-2-ene, but that in the case of 1,2,4-trifluorobenzene⁶⁵, the tetrafluorobenzenes⁶⁶, and possibly the penta-⁶⁷ and hexa-fluorobenzenes³⁸, triplet quenching does not occur. There is doubt about the last two compounds in that sensitized *cis-trans* isomerization of the but-2-ene occurs^{38,40}, but this may involve a chain mechanism⁴⁰.

As has been pointed out in a recent report¹⁴, the efficiency of energy transfer from the triplet state of an aromatic molecule to but-2-ene will depend upon the relative triplet energies of the collision pair. The energy of the triplet state of *cis*-but-2-ene, measured by the oxygen perturbation method¹²¹⁻¹²⁴ has been given as 78.22 kcal mol⁻¹ (3.40 eV)¹⁴. It might be expected from the experimental data given in Table 2 that the triplet states of tetra-, penta- and hexa-fluorobenzenes would not be quenched by but-2-ene, but that the fluoro- and difluoro-would be, with the trifluoro-benzenes a marginal case. Since triplet 1,3-difluorobenzene is apparently strongly quenched by but-2-ene, the value of its triplet energy given in Table 2 is probably in error, especially since the value differs markedly from the calculated value. However, further difficulties have been pointed out in that in cases where energy conditions are apparently favourable for quenching, quenching is nevertheless inefficient¹⁴. There are other peculiarities concerning quenching of the triplet states of substituted benzenes in this respect. It was found that 1,3- and 1,4-bis(trifluoromethyl) benzenes gave rise to a preferred *cis* to *trans* sensitized isomerization of but-2-ene, whereas most other donors studied, including 1,2-; 1,3-; and 1,4-fluoromethyl benzenes gave no preferred geometrical

TABLE 16

QUENCHING OF TRIPLET STATES OF SUBSTITUTED BENZENES BY BIACETYL AND ADDITIVES

Aromatic molecule	Quencher	k_B/k_Q^a	Reference
	<i>cis</i> -but-2-ene	3.8	110
	<i>cis</i> -but-2-ene	12.4	17
	<i>cis</i> -but-2-ene	51.2 ^b	87
	<i>cis</i> -but-2-ene	18.3 ^b	87
	<i>cis</i> -but-2-ene	44.5 ^b	87
	<i>cis</i> -but-2-ene	3.64	105
	<i>cis</i> -but-2-ene	16.7	120
	<i>cis</i> -but-2-ene	2.11	105
	<i>cis</i> -but-2-ene	7.93	105
	<i>cis</i> -but-2-ene	36,3 ^b	105
	<i>cis</i> -but-2-ene	38.0 ^b	105
	But-1,3-diene	0.183	110
	But-1,3-diene	0.10	30
	But-1,3-diene	0.023	105
	But-1,3-diene	0.027	105
	But-1,3-diene	0.0081	105

^a k_B is rate constant for quenching of triplet aromatic by biacetyl, k_Q that for quenching by additive.

^b Values not corrected for singlet quenching which may be significant.

isomerization. It was speculated that for aromatic donors with energy levels close to that of the but-2-ene, *cis* to *trans* isomerization might be a preferred route. However, Table 3 shows that although the triplet energy of 1,4-bis(trifluoromethyl) benzene is indeed close to that of but-2-ene, that of 1,3-bis(trifluoromethyl) benzene is similar to that of benzene itself, and moreover, the energies of the fluorotoluenes, which give normal sensitized isomerization in the but-2-ene are themselves close to that of but-2-ene. It is evident therefore that the reason for anomalous behaviour of the CF_3 -substituted benzenes is not solely connected with the relative energies of the triplet states. The marked variation in efficiency of quenching of the excited states of the fluorobenzenes by buta-1,3-diene also warrants further consideration.

OTHER SUBSTITUENTS

No systematic study of other substituted benzenes has been carried out. The fluorescence and intersystem crossing yields in perdeuteriobenzene have been reported¹²⁵. In solution monohalobenzenes with the exception of fluorobenzene have been shown to undergo efficient cleavage to give a phenyl radical and halogen atom¹²⁶⁻¹²⁹.

Aniline vapour has a well-resolved vibronic absorption spectrum in the region of the first excited singlet transition. By means of high-resolution phase fluorimetry the spectrum of fluorescence lifetimes and quantum yields have been determined over the region from 300 to 275 nm with a bandwidth of 2.7 Å¹³⁰. Quantum yields fluctuate between 0.3 and 0.6 and the reciprocal lifetime, $1/\tau$, varies in the range $(1.3-2.3) \times 10^8 \text{ s}^{-1}$. $1/\tau$ shows sharply pointed minima whereas the quantum yields have maxima at the wavelengths of all major absorption peaks. The calculated intersystem crossing rate constants k_{isc} have minimum values at these wavelengths (Fig. 5).

The observed correspondence between the absorption spectrum and the two rate constants, k_f and k_{isc} may be understood from the following general point of view. The appearance of a discrete structure in the low-pressure gas-phase absorption spectrum of large molecules can be correlated with molecular symmetry which imposes selection rules on certain vibronic transitions, both radiative and radiationless. In aniline, the optical transition between the ground state and the lowest excited singlet state is electronically allowed and, hence, k_f is large ($\sim 10^{10} \text{ s}^{-1}$) and shows relatively small variation with excitation energy. The symmetry selection rules apply in this case to intersystem crossing which proceeds *via* spin-orbit and vibronic coupling simultaneously. The experimental results for k_{isc} suggest that intersystem crossing transitions are symmetry forbidden for just those vibronic modes which correspond to the discrete bands in the absorption spectrum. This suggestion is supported by the data available for *N*-methylaniline and *NN*-dimethylaniline: the symmetry of the aniline molecule is destroyed, the absorption spectrum

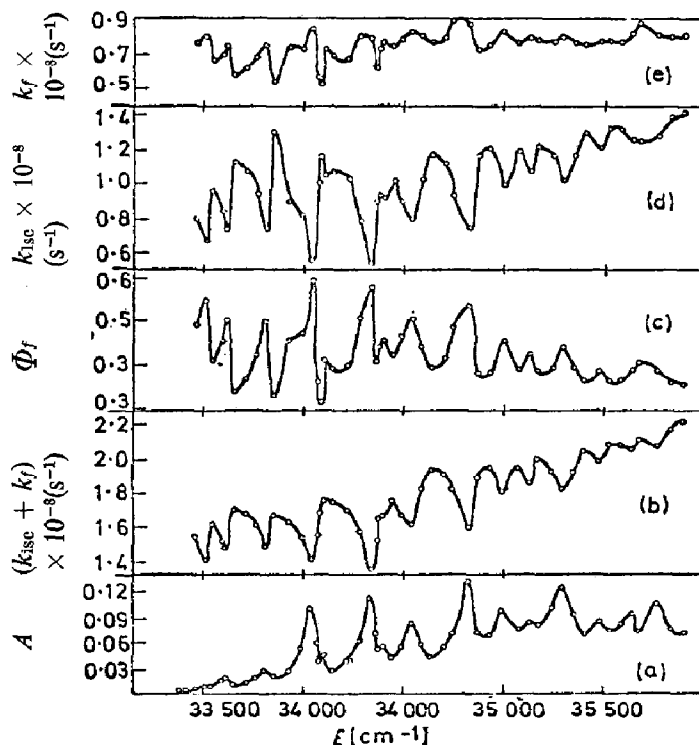


Fig. 5. Spectral data of aniline vapour in the collision-free region: (a) absorbance as measured on a Cary 14 spectrophotometer; (b) reciprocal lifetime $1/\tau = k_f + k_{isc}$; (c) fluorescence quantum yield; (d) intersystems crossing rate constant; (e) fluorescence emission rate constant. Reproduced with permission from *J. Chem. Phys.*, 54 (1971) 2387.

becomes structureless and, at the same time, the life-times and quantum yields become smooth functions of energy¹³⁰.

Aniline may be regarded as belonging to the C_{2v} symmetry group. The ground-state species is A_1 and the first excited singlet state is a B_2 species. There are two triplet states which have energies lower than the 1B_2 state: the lowest one, 3A_1 , located at $26,800\text{ cm}^{-1}$ and a higher one, a 3B_2 state. The energy of this state is not known exactly but is probably located just below the 1B_2 state. According to the selection rules for first-order spin-orbit coupling, species of like symmetry in the C_{2v} group cannot mix by first-order spin-orbit coupling. Consequently, the states $^1B_2(S_1)$ and $^3A_1(T_1)$ couple by first-order spin-orbit interaction but this process would be unspecific with respect to vibronic symmetry species. Also, the transition $S_1 \rightarrow T_1$ is expected to be relatively inefficient because of the large energy gap, $E(S_1) - E(T_1) \approx 7200\text{ cm}^{-1}$. On the other hand, the transition $^1B_2(S_1) \rightarrow ^3B_2(T_2)$, which would be favourable with regard to the small energy gap, is forbidden in first order; it may, however, be induced by second-order processes involving both spin-orbit and vibronic coupling. In aniline the major absorption peaks are due to either totally symmetric (a_1) modes or (b_1) modes. If a molecule

TABLE 17

QUANTUM YIELDS AND RATE CONSTANTS FOR INDIVIDUAL QUANTUM LEVELS OF ANILINE

Level		$(k_{ise} + k_f) \times 10^{-8}(\text{s}^{-1})$	$k_f \times 10^{-8}(\text{s}^{-1})$	$k_{isc} \times 10^{-8}(\text{s}^{-1})$
0	0.68	1.36	0.92	0.44
6a ¹	0.58	1.46	0.85	0.61
1 ¹	0.655	1.24	0.81	0.43

is excited selectively to one of these modes or a combination of them, vibronic coupling should be very small according to the selection rule above, and thus k_{isc} should be at a minimum. Some rate constants for individual levels are given in Table 17¹³⁰.

SUMMARY

The points of interest prompted by this survey may be summarized as follows.

(1) For the fluoro- and trifluoro-methyl substituents, integration of area under absorption curves does not lead to realistic values for the radiative lifetime of the singlet states.

(2) For all substituted benzenes studied systematically there is a correlation between the value of the radiative lifetime and the perturbations to orbital symmetry produced by the number and positions of the substituents.

(3) In methyl benzenes the value of the non-radiative decay rate constant is approximately constant, whereas for other substituted groups this is not the case, reflecting the change in geometry in excited states of heavily substituted compounds.

(4) For all compounds molecular orbital calculations indicate the presence of triplet states intermediate in energy between the first singlet and lowest triplet. The role of these intermediate levels, and the nature of the non-radiative decay process in substituted benzenes should be probed.

(5) For substituted benzenes redistribution of vibrational energy is an extremely efficient process, being unimolecular in some cases whereas it is collisional in benzene. A study of such redistribution processes as a function of complexity of the molecule would be advantageous.

(6) The quenching of the excited singlet states of substituted benzenes by singlet electronic energy acceptors is extremely efficient, and may indicate a contribution to the total efficiency of Forster resonance long-range transfer.

Further systematic studies of these effects are necessary.

(7) The quenching of the excited triplet states of substituted benzenes is not explained simply on the basis of the calculated and observed energy level data at present available. There is great need for very accurately determined energy level data, and systematic studies of energy transfer from a larger range of donors and acceptors to adequately establish the mechanism.

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Notes added in proof (September 21, 1972)

To page 103: Since the submission of this article, a study of the quantum yields and decay times in C_6H_6F and C_6D_6 has been published¹³².

To page 119: It has recently been suggested that non-radiative conversion to a $\sigma\pi^*$ state of benzene may be the Channel III process¹³³.