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QUENCHING OF SINGLET AND TRIPLET EXCITED AROMATIC HYDROCARBONS BY SULPHIDES:- THE AMINE AND SULPHIDE ENHANCED PHOTO-INDUCED DEGRADATION OF CHLORO- AND CYANOAROMATIC HYDROCARBONS.

R.A. Beecroft, R.S. Davidson, D. Goodwin and J.E. Pratt

Department of Chemistry, The City University,
Northampton Square, London EC1V OHB

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Abstract- Sulphides have been shown to be capable of quenching the excited singlet and triplet states of several aromatic hydrocarbons and their derivatives. The quenching is proposed to involve an electron transfer mechanism. The use of sulphides and amines to generate aromatic hydrocarbon radical cations from the excited states of these compounds has been utilised in order to carry out reductive decyanation reactions of cyanoaromatic hydrocarbons.

There have been many reports pertaining to the mechanism of the amine assisted photo-induced dehalogenation of halo-aromatic hydrocarbons [1,2,3]. Although there is considerable evidence [3,4,5] that such reactions proceed via an electron transfer mechanism, of the type outlined in Scheme 1, the identity of the excited states of the aromatic hydrocarbon which are able to undergo electron transfer reactions with the amine has remained a subject for debate. It has been generally assumed that the reactions occur via the singlet state, which is known to be susceptible to quenching by amines. The suggestion [6,7] that these reactions can involve both singlet and triplet states has been supported by the recent report [8] that amines can quench both the singlet and triplet excited states of chloroaromatic hydrocarbons.

Diethyl sulphide has been found [9] to be capable of assisting the photo-induced dehalogenation of halo-aromatic hydrocarbons in an analogous manner to amines. Evidence that the parent aromatic hydrocarbons can undergo electron transfer reactions with sulphides was also reported [9]. In order to gain an insight into the mechanism of these reactions it is necessary to determine the ability of sulphides to quench the excited states of aromatic hydrocarbons. We now report the results of such an investigation. As organic sulphides are known to undergo electron transfer reactions with 9,10-dicyanoanthracene (DCA) [10, 11], which has been used to sensitise their photo-oxidation (Scheme 2), the interaction of sulphides with the excited states of several cyanoaromatic hydrocarbons has also been investigated.

$$\begin{aligned}
\mathrm{ArCl^{*} + Et_3N} &\longrightarrow \mathrm{ArCl^{\overline{\bullet}} + Et_3\overset{+\bullet}{N}} \\
\mathrm{ArCl^{-}} &\longrightarrow \mathrm{Ar\bullet + Cl^{-}} \\
\mathrm{Cl^{\overline{\bullet}} + Et_3\overset{+\bullet}{N}} &\longrightarrow \mathrm{HCl + Et_2N\dot{C}HMe} \\
\mathrm{Ar\bullet + Et_3N} &\longrightarrow \mathrm{ArH + Et_2N\dot{C}HMe}
\end{aligned}$$

Scheme 1

$$\begin{aligned}
\mathrm{DCA^{*} + R_2S} &\longrightarrow \mathrm{DCA^{\overline{\bullet}} + R_2S^{+\bullet}} \\
\mathrm{DCA^{\overline{\bullet}} + O_2} &\longrightarrow \mathrm{DCA + O_2^{\overline{\bullet}}} \\
\mathrm{R_2S^{+\bullet} + O_2^{\overline{\bullet}}} &\longrightarrow \mathrm{products}
\end{aligned}$$

Scheme 2

1. QUENCHING OF THE EXCITED STATES OF AROMATIC HYDROCARBONS BY SULPHIDES

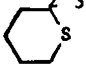
Results and Discussion

The results in Table 1 reveal that both cyclic and acyclic sulphides quench the fluorescence of a range of aromatic hydrocarbons and their cyano-derivatives. The finding that the fluorescence quenching is more efficient in acetonitrile than in the non-polar solvents indicates that the quenching involves an electron transfer process. Steric effects upon the quenching are illustrated by the efficiency with which di-butyl sulphides quench the fluorescence of a range of aromatic hydrocarbons, i.e. $n\text{-}Bu_2S > s\text{-}Bu_2S > t\text{-}Bu_2S$. In more polar solvents electron transfer can take place over greater distances, so the importance of steric hindrance to electron transfer will be less in polar compared with non-polar solvents. Consequently, the finding that these steric effects are most marked in the non-polar solvents (Table 1) is consistent with an electron transfer process. It has been reported [12] that di-t-butyl substitution of the amine retards the dissociation of pyrene - N,N-dimethylaniline exciplexes and thereby increases the equilibrium constant for reversible exciplex formation by these compounds. This behaviour was attributed [12] to the effect of amine substituents upon the entropies of solvation of the exciplexes and the transisition states involved in their formation and decomposition. Similarly, the observed trend in the abilities of di-butyl sulphides to quench the fluorescence of aromatic hydrocarbons can be attributed to a steric effect upon the equilibrium constant for intermediate reversible exciplex formation.

Using the technique of laser flash photolysis it was found that diethyl sulphide, like amines, is capable of quenching the triplet states of a variety of aromatic hydrocarbons (Table 2). However, the triplet quenching by diethyl sulphide (Table 2) was found to be less efficient than that caused by tertiary amines [8]. This probably reflects the higher ionisation potential of the sulphide. When the range of sulphides was extended, it was found that the quenching of triplet aromatic hydrocarbons by sulphides is a widespread phenomenon (Table 3 and 4). A steric effect, analogous to that upon the fluorescence quenching, was observed upon the efficiency with which di-butyl sulphides quench triplet aromatic hydrocarbons. The observed increase in the efficiency with which diethyl sulphide quenches triplet biphenyl on changing the solvent from cyclohexane to acetonitrile (Table 2) is consistent with the involvement of an electron transfer quenching process.

Acyclic disulphides of the type $MeS(CH_2)_n SMe$ were found to quench both the singlet and triplet excited states of 1-cyanonaphthalene (Tables 1 and 4) more efficiently when $n=3$ than when $n=2$. As a consequence of interactions between the two sulphur atoms [13], the radical cations of disulphides are often more stable than the corresponding mono-sulphides. By analogy with intramolecular exciplex formation [14,15,16], unfavourable eclipsing interactions in the linking polymethylene chain (which disfavour the adoption of conformations in which the two sulphur atoms can interact) would be expected to be more important when $n=2$ rather than 3. Thus the ability of disulphides to quench the excited states of aromatic hydrocarbons would appear to be determined by the relative stability of the sulphide radical cations.

Table 1. Stern-Volmer constants (K_{SV}) for quenching of the fluorescence of a range of aromatic hydrocarbons by sulphides in both polar and non-polar solvents, under degassed conditions.

Aromatic Hydrocarbon	Sulphide	K_{SV} (M^{-1})	
		Acetonitrile	Cyclohexane
Biphenyl	Et_2S	65	16.7
"	n-Bu_2S	101.7	21.9
"	s-Bu_2S	21.2	2.8
"	t-Bu_2S	15.7	1.6
"	$MeS(CH_2)_2SMe$	121.9	39.5
Naphthalene	Et_2S	1.9	a
9-Cyanoanthracene	Et_2S	4.8	a
"	Ph_2S	26	a
"	MeSPh	15.5	a
9,10-Dicyanoanthracene	Et_2S	243	a
"	MeSPh	26.7	a
4-Cyanobiphenyl	Et_2S	37	a
1-Cyanonaphthalene	Me_2S	131	120
"	Et_2S	125	87
"	n-Bu_2S	143	85
"	s-Bu_2S	115	30
"	t-Bu_2S	80	3.9
"	$MeS(CH_2)_2SMe$	137	78
"	$MeS(CH_2)_3SMe$	166	95
"		145	95.6
"	1,3-Dithiane	122	112
"	1,4-Dithiane	104	58.8

*where a not determined

Table 2. Rate constants for quenching of triplet aromatic hydrocarbons by diethyl sulphide in acetonitrile and in cyclohexane solutions, under degassed conditions.

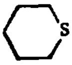
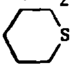
Aromatic Hydrocarbon	Solvent	K_q^T (M^{-1} s^{-1})
Biphenyl	CH_3CN	1.04×10^7
"	C_6H_{12}	4.83×10^6
4-Chlorobiphenyl	CH_3CN	5.87×10^6
Naphthalene	"	1.89×10^6
1-Chloronaphthalene	"	5.76×10^6
1-Cyanonaphthalene	"	1.98×10^7

Table 3 Effects of added sulphide upon the triplet yield and triplet lifetimes for a range of aromatic hydrocarbons in acetonitrile and cyclohexane solutions under degassed conditions.

Aromatic Hydrocarbon	Sulphide	Sulphide Concentration (M)	Solvent	OD	1 (μs)	2 (μs)
Biphenyl	None	0	CH_3CN	0.473^d	5.84	7.54
"	n-Bu_2S^b	3.28×10^{-3}	"	0.515^d	2.53	7.67
"	s-Bu_2S^b	1.57×10^{-2}	"	0.477^d	3.01	7.19
"	t-Bu_2S^b	6.37×10^{-2}	"	0.507^d	3.55	6.74
Biphenyl	None	0	CH_3CN	0.580^d	5.10	7.44
"	Et_2S^c	1.54×10^{-2}	"	0.612^d	2.36	4.10
"	$MeS(CH_2)_2SMe^c$	8.2×10^{-3}	"	0.559^d	1.69	3.27
Biphenyl	None	0	C_6H_{12}	0.581^d	11.41	-
"	Et_2S^c	5.98×10^{-2}	"	0.622^d	2.53	4.49
"	$MeS(CH_2)_2SMe^c$	2.53×10^{-2}	"	0.612^d	2.20	3.96
4-Chlorobiphenyl	None	0	CH_3CN	0.638^e	4.44	6.79
"	Et_2S	1×10^{-2}	"	0.592^e	2.76	4.42
4-Chlorobiphenyl	None	0	C_6H_{12}	0.597^e	7.74	11.62
"	Et_2S	1×10^{-2}	"	0.569^e	5.41	8.33

a - Optical density of triplet-triplet absorption spectrum at its maximum intensity; b - sufficient sulphide to quench 25% of the biphenyl fluorescence; c - sufficient sulphide to quench 50% of the biphenyl fluorescence; d - λ = 358 nm; e - λ = 372 nm.

Table 4 Effects of added sulphides upon the yield and lifetime of 1-cyanonaphthalene triplets in acetonitrile and cyclohexane solutions, under degassed conditions.

Sulphide^a	Sulphide Concentration (M)	Solvent	OD^b (414 nm)	τ_1 (μs)	τ_2 (μs)
None	0	CH_3CN	0.099	4.63	9.76
n-Bu_2S^c	2.33×10^{-3}	"	0.155	2.88	6.41
s-Bu_2S^c	2.9×10^{-3}	"	0.153	3.08	7.22
t-Bu_2S^c	4.16×10^{-3}	"	0.158	2.67	6.89
None	0	CH_3CN	0.168	3.03	5.13
$MeS(CH_2)_2SMe^d$	7.3×10^{-3}	"	0.171	1.67	11.54
$MeS(CH_2)_3SMe^d$	6.02×10^{-3}	"	0.132	1.48	7.52
 ^{d}	6.89×10^{-3}	"	0.177	1.94	5.01
1,4-dithiane	9.6×10^{-3}	"	0.128	1.92	7.91
None	0	C_6H_{12}	0.173	5.53	8.76
Et_2S^d	1.15×10^{-2}	"	0.277	2.44	6.24
n-Bu_2S^d	1.17×10^{-2}	"	0.370	2.54	7.07
s-Bu_2S^d	3.33×10^{-2}	"	0.252	2.08	6.09
$MeS(CH_2)_2SMe^d$	1.28×10^{-2}	"	0.228	1.59	3.05
$MeS(CH_2)_3SMe^d$	1.05×10^{-2}	"	0.222	1.05	2.24
 ^{d}	1.05×10^{-2}	"	0.273	2.87	6.88

a - in some cases the sulphides acted as light filters; b - optical density at the wavelength of maximum triplet-triplet absorption; c - sufficient sulphide to cause 25% quenching of 1-cyanonaphthalene fluorescence; d - sufficient sulphide to cause 50% quenching of 1-cyanonaphthalene fluorescence.

It can be seen from the results in Tables 3 and 4 that the presence of sulphides not only results in triplet quenching but also causes an enhancement of the quantum yield of triplet production (as determined from the magnitude of the triplet-triplet absorption at the wavelength of maximum absorption at t=0). As the sulphides are also behaving, to varying extents, as light filters the absolute enhancement of intersystem crossing by the sulphides is unknown. Such an enhancement of triplet production provides evidence for intermediate exciplex formation between the sulphide and the singlet excited aromatic hydrocarbon. A possible mechanism for sulphide enhanced triplet production is outlined in Scheme 3.

$$\begin{tikzcd}
D \arrow[r] & D^* \arrow[r] & (D...S)^* \arrow[rr] \arrow[dr] & & (D^{-\bullet}\ S^{+\bullet}) \arrow[dr] & \\
 & & & {}^3D^* + S & & D^{-\bullet} + S^{+\bullet} \arrow[ll]
\end{tikzcd}$$

Scheme 3

Decay of the initial encounter complex, the equilibrium exciplex or recombination of solvent separated radical ions could all lead to triplet production. Quenching of triplet aromatic hydrocarbons by sulphides may also involve intermediate exciplex formation, as outlined in Scheme 4, and could lead to radical ion production in polar solvents.

$$D^* + S \longrightarrow (D^*...S) \longrightarrow (D^{-\bullet} S^{+\bullet})^*$$

Scheme 4

Although there has been a recent report [17] that DCA undergoes substrate enhanced intersystem crossing in the presence of thioanisole, no quantitative data was provided in support of this claim. Laser flash photolysis experiments, similar to those reported above, using solutions of DCA containing sufficient quantities of thioanisole, diphenyl sulphide or diethyl sulphide to cause either 50% or total fluorescence quenching, failed to show any significant enhancement in the yield of triplet DCA. However, due to the low extinction coefficient of the triplet-triplet absorption of DCA, we would not have been able to detect small (<10%) enhancements of triplet production.

Conclusions

A range of sulphides are capable of quenching both the singlet and triplet excited states of a variety of aromatic hydrocarbons and their derivatives. All the results, including the observed enhancement of intersystem crossing in the presence of sulphides, are consistent with the formation of a charge-transfer complex between the sulphide and the excited aromatic hydrocarbon.

The observation that sulphides quench triplet aromatic hydrocarbons is consistent with recent results obtained by Davidson and co-workers [8] which indicate that a range of cyclic and acyclic amines are capable of quenching the triplet states of aromatic hydrocarbons in acetonitrile solution. Consequently, the possibility arises that the diethyl sulphide enhanced photo-induced dehalogenation of aryl aromatic hydrocarbons may involve interactions between the sulphide and both the excited singlet and triplet states of the hydrocarbon.

From the above results it can be seen that sulphides exhibit behaviour analogous to amines in their ability to quench the excited states of aromatic hydrocarbons. Both amines [14,15,16] and sulphides have been shown to quench the fluorescence of cyanoaromatic hydrocarbons. It would therefore seem

Table 5 Extent of consumption of substrate and deuterium incorporation into the substrate and product aromatic hydrocarbon upon irradiation of cyano-aromatic hydrocarbons (0.05g/15 mls) in the presence of electron donors (1 ml/15 mls) in a CH_3CN/D_2O (5:1 v/v) solvent mixture

Substrate	Electron donor	Substrate consumed (%) 20 hrs	Yield[a] of aromatic hydrocarbon (%) 20 hrs	(%) One deuterium incorporation		
				Substrate 20 hrs	Aromatic hydrocarbon 4 hrs	20 hrs
1-Cyanonaphthalene	Et_2S	46.6	<4	0	b	b
"	NEt_3	>95	<4	43.5	(M+2)[c]	(M+3)[c]
"	DMP	14.3	<4	1.7	b	b
"	DABCO[d]	19.4	<4	0	b	b
4-Cyanobiphenyl	Et_2S	25.5	21.8	0	25.3	40.1
"	NEt_3	>95	14.2	(M+4)	b	51.8
"	DMP	12.1	4.7	0	0	1.7
9-Cyanoanthracene	Et_2S	70.1	<4	2	b	b
"	NEt_3	>95	<4	71	b	(M+4)[c]
"	DMP	89.2	10.3	0	b	84.6
9-Cyanophenanthrene	Et_2S	45.1	7.5	(M+4)[c]	b	16.4
"	NEt_3	>95	<4	(M+4)[c,e]	b	b
9,10-Dicyanoanthracene	Et_2S	0	0	0	b	b
"	NEt_3	0	0	0	b	b
4-Cyanopyridine	Et_2S	38.8	<4	0.7	b	8.1
"	NEt_3	>95	<4	25.6	b	b

Where DMP = N,N-dimethylpiperazine; DABCO = 1,4-diazabicyclo[2,2,2]octane; a - based on amount of substrate present prior to irradiation; b - insufficient hydrocarbon to be detected; c - most intense peak; d - 0.28 g/15 mls and e - 4 hrs irradiation.

Table 6 Deuterium incorporation into anthracene (0.01g/15 mls) as a result of photolysis in the presence of triethylamine and N,N-dimethylpiperazine (DMP) (both 1 ml/15 mls) in a CH_3CN/D_2O (5:1 v/v) solvent mixture for 20 hrs

Electron donor	Relative peak intensity (%)								
	Mass ion	M+1	M+2	M+3	M+4	M+5	M+6	M+7	M+8
NEt_3	14.3	34	63.3	85.2	100	90.1	44.8	14.2	3.1
DMP	11.7	21.5	49	100	81	63.4	24.5	8.2	1.8

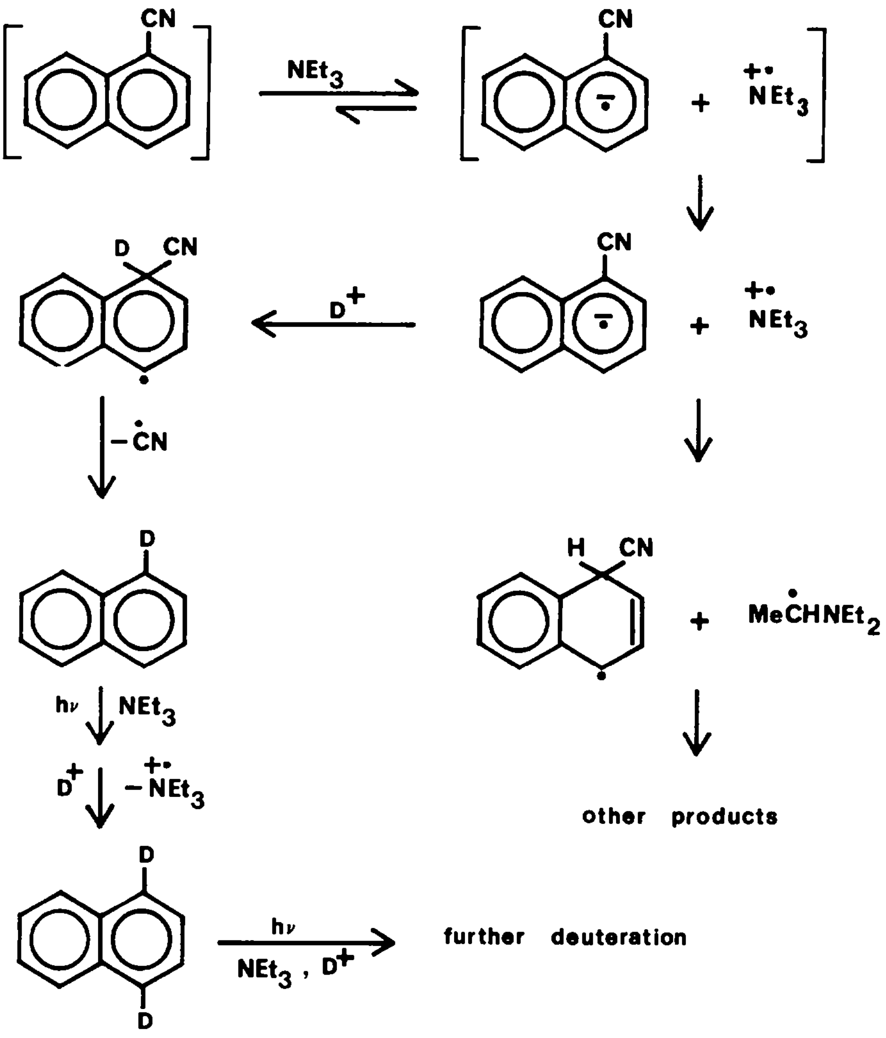
reasonable to suggest that amines, like sulphides, may be capable of quenching the triplet states of cyanoaromatic hydrocarbons. Consequently, it was of interest to study the interactions of these compounds under degassed conditions. In particular to determine whether they would lead to decyanation of the hydrocarbons.

2. AMINE AND SULPHIDE ENHANCED PHOTO-REDUCTIVE DECYANATION OF CYANO-AROMATIC HYDROCARBONS

Results and Discussion

Irradiation of several aromatic hydrocarbons was carried out in the presence of amines and sulphides in an acetonitrile-deuterium oxide (5:1) solvent mixture. In all cases the cyanoaromatic hydrocarbons were consumed (Table 5). Deuterium incorporation into the photo-produced aromatic hydrocarbons was observed in several of the reactions and provides evidence [4,18] for the involvement of radical ions in these reactions. In contrast to the analagous reactions of aryl halides [4,9] deuterium incorporation into the substrate was sometimes observed (Table 5). This finding indicates that in such cases the processes leading to electron transfer between the electron donor and the cyanoaromatic hydrocarbon must be reversible. The trend in the rate constants for the fluorescence quenching of 9-cyanophenanthrene by amines has been shown [19] to be consistent with reversible exciplex formation.

In some cases extensive deuterium incorporation into the product aromatic hydrocarbon was observed (Tables 5 and 6). This deuterium incorporation could either occur via interaction of the intermediate radical ions with the solvent or by further reaction of the photo-produced aromatic hydrocarbon with the electron donors. The finding (Table 6) that irradiation of anthracene in the presence of either triethylamine or N,N-dimethylpiperazine (DMP) resulted in considerable deuterium incorporation into the hydrocarbon reveals that anthracene is capable of undergoing electron transfer reactions with amines. A mechanism of the type outlined in Scheme 5 (for the reaction between 1-cyanonaphthalene and triethylamine) is consistent with the above results. When anthracene or it's derivatives were used in these reactions dimerisation effectively competed with interactions between the excited anthracene compound and the electron donor. Crystals of the dimers were formed during irradiation and identified by comparison with authentic samples. The stability of DCA does not reflect the efficiency (Table 1) with which diethyl sulphide quenches the fluorescence of DCA. It would therefore appear that the formation of excited complexes between the excited states of DCA and the electron donors merely results in energy wastage. The discrepancy between the consumption of substrate and the low yields of parent aromatic hydrocarbon, obtained when triethylamine is used as the electron donor is attributed to proton transfer from the amine radical cation to the radical anion of the cyanoaromatic hydrocarbon (Scheme 6). The addition of the α-C-H bond of triethylamines to arenes has also been attributed to a mechanism involving electron transfer followed by proton transfer [20]. In the presence of 1,4-diazabicyclo[2,2,2]octane, which does not contain any readily abstractable α-hydrogen atoms, the photolysis of 1-cyanonaphthalene did not lead to such a marked consumption of the aromatic hydrocarbon. It would therefore appear that 1-cyanonaphthalene abstracts a proton from triethylamine more readily than it abstracts a deuteron from the solvent. The photolysis of 9-cyanophenanthrene in the presence of triethylamine in both benzene and acetonitrile solutions has been reported [19] to yield 9,10-dihydrocyanophenanthrene as the major product. Under the conditions used in this study, any dihydro products derived from the cyanoaromatic or photo-produced parent aromatic hydrocarbons could contain deuterium atoms. Consequently, the values for deuterium incorporation into the substrate and product aromatic hydrocarbon will be misleadingly high if dihydro products are being generated.



Scheme 5

Conclusions

A range of cyanoaromatic hydrocarbons can undergo electron transfer reactions with a variety of electron donors to yield radical ions. In some cases decyanation took place to yield the parent aromatic hydrocarbons. The yields were found to be considerably lower if the radical anion of the substrate is capable of abstracting a proton from the electron donor. From the earlier results it is clear that radical ion formation can take place as a consequence of interactions between the donor and the excited singlet and triplet states of the cyano-aromatic hydrocarbon. However, no evidence has been obtained to distinguish which of these interactions are involved in the decyanation process.

EXPERIMENTAL

Fluorescence spectra were recorded on a Perkin Elmer MPF-4 spectrofluorimeter. Laser flash photolysis experiments were carried out with an excimer laser (Oxford Lasers) using a procedure which has been previously described [21]. GC-mass spectra were recorded on a Kratos MS 30 spectrometer (connected to a DS-50-S data system) operating at 70 eV, attached to a Pye 104 gas chromatograph fitted with a 10% SE 30, chromosorb W, 60-80 mesh column. GLC analyses were recorded on a Perkin Elmer Sigma 3 gas chromatograph using a Perkin Elmer 10% SE 30, chromosorb W, 60-80 mesh, column. IR spectra were recorded on a Perkin Elmer 402 spectrometer. The following chemicals were used as supplied:- 4-chlorobiphenyl, 9-cyanoanthracene, 9-cyanophenanthrene, 9-cyanopyridine, di-n-butyl sulphide, di-s-butyl sulphide, di-t-butyl sulphide, N,N-dimethylpiperazine, 1,3-dithiane, 1,4-dithiane, diethyl sulphide, diphenyl sulphide, thioanisole, triethylamine (all Aldrich), anthracene, naphthalene, phenanthrene (BDH), argon (BOC, zero-grade), 9,10-dicyanoanthracene (Eastman Kodak), acetonitrile (Fisons, AnalaR), deuterium oxide (Goss), 1-chloronaphthalene, 1-cyanonaphthalene and 1,4-diazabicyclo[2,2,2]octane (Ralph N. Emanuel). Pyridine (Fisons) was distilled prior to use. The following spectroscopic solvents were used as supplied:- acetonitrile (Aldrich, Gold Label) and cyclohexane (Hopkin and Williams, Spectrosol R). Biphenyl (BDH) was recrystallised prior to use. We thank Mr. S. Faruki for the samples of 1,2-dimethyl-1,2-dithioethane, 1,2-dimethyl-1,3-dithiopropane (both distilled prior to use) and pentamethylene sulphide. Authentic samples of the dimers of the anthracene compounds were prepared by irradiation of these compounds in degassed toluene solution, within a circular array of 16 Sylvania (8W, F8T5/BLB) black-light fluorescent lamps, whch have a maximal output at 350 nm, for 12 hours. The crystals obtained were filtered, washed with toluene and dried. 4-Cyanobiphenyl was prepared from 4-chlorobiphenyl using the procedure reported by House and Fischer [22] for the coversion of 2-chloronaphthalene to 2-cyanonaphthalene. The 4-cyanobiphenyl was obtained in 45% yield by distillation (under reduced pressure) of the crude product. The structure of the product was confirmed by its spectral and physical characteristics.

Photophysical measurements

Fluorescence quenching experiments were carried out using solutions of the aromatic hydrocarbons which were sufficiently concentrated to have an optical density of 0.1 at the excitation wavelength when diluted by a factor of 10. Degassing was achieved by flushing the solutions with a stream of argon for 5 mins and stoppering the cell. The effect of adding increasing amounts of a quencher was determined by monitoring the resultant change in the intensity of the uncorrected fluorescence spectra.

For the laser flash photolysis experiments, stock solutions of the aromatic hydrocarbons and their derivatives were made up to an optical density of 1.0 at the excitation wavelength (249 nm, krypton fluoride or 353 nm, xenon fluoride). Appropriate amounts of quencher were added to each solution. The solutions were then degassed by three freeze-pump-thaw-shake cycles. The triplet-triplet absorption spectra obtained as a result of flash photolysis of these solutions was photographed and the information digitised using a Tektronix 4662 interactive digital plotter and analysed by computer. For cases where two components contributed to the decay curve the initial and final sections of the decay curve were analysed separately.

The rate constant for the triplet quenching (Kq) was calculated from the slope of a plot of the triplet lifetime against quencher concentration.

Photolysis Reactions

Solutions of the aromatic hydrocarbons, containing the appropriate electron donor, were placed in quartz photolysis tubes, flushed with a stream of argon for 30 mins and then stoppered. The solutions were then irradiated within a circular array of 12 Sylvania G15T8 lamps which have a maximum output at 254 nm. Samples were taken after 0, 4 and 20 hrs irradiation. The loss of substrate and appearance of products were followed by GLC analysis. The aromatic hydrocarbon products were identified using GLC analysis (by comparison with authentic samples) as well as by GC/mass spectral analysis. Any crystals formed during the photolysis of anthracene derivatives were identified by comparison with the appropriate dimers, using IR spectroscopy.

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