Excited Complex Formation between Heterocyclic Compounds and Aromatic Hydrocarbons and Amines

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Many aromatic hydrocarbons in their excited singlet states form fluorescent exciplexes with heterocyclic compounds, *e.g.* furans, thiophens, pyrroles, and indoles. Dipole moments and enthalpies of formation for some of the exciplexes have been determined. In those cases where fluorescent exciplex formation was not observed, quenching rate constants were measured. Rate constant for the quenching of the excited singlet states of 2,4,5-triphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole by some amines have been measured and in some of the systems, fluorescent exciplex formation observed.

It is now recognised that the photochemistry of many compounds is determined by their propensity for undergoing excited state redox reactions.[1,2] Parameters which affect these reactions include the energy of the excited state, the oxidation potential of the donor, and the reduction potential of the acceptor molecule.[3] Donor–acceptor interactions can lead to quenching of excited states, enhanced intersystem crossing, emissive excited complexes, and photochemical reactions. By use of fast reaction techniques, *e.g.* pico- and nanosecond flash and fluorescence spectroscopy, it has been possible to show that the initially formed encounter complex and the solvent relaxed complexes play distinct and different roles.[4] It is particularly difficult to ascertain in those systems which exhibit fluorescent exciplex formation and chemical reactivity whether the reaction occurs *via* the fluorescent species or *via* the non-fluorescent encounter complex. At least the observation of an emissive complex whose wavelength of emission is solvent sensitive establishes that there is a charge-transfer interaction in the excited state. When the reaction between two molecules does not lead to an emissive complex it becomes much more difficult to establish whether they are reacting by a charge-transfer process. Usually the effect of changing a substituent on either the donor or acceptor molecules upon the rate

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[1] R. S. Davidson, in 'Molecular Association,' ed. R. Foster, Academic Press, London, 1975, vol. 1, p. 216.

[2] A. Lablache-Combier, *Bull. Soc. chim. France*, 1972, 4791.

[3] H. Beens and A. Weller, in 'Organic Molecular Photophysics,' ed. J. B. Birks, Wiley, London, 1975, vol. 2, p. 159.

[4] M. Ottolenghi, *Accounts Chem. Res.*, 1976, **6**, 153.

constant for quenching (k_q) is examined and if there is a linear correlation between log k_q and the appropriate redox potentials the quenching by a charge-transfer process is inferred.

There is a growing number of examples of photoreactions of heterocyclic compounds which appear to involve excited state redox reactions. These include the reaction of furan[5] and pyrrole[6] with benzene, pyrrole with naphthalene,[7] furan with 1-cyanonaphthalene,[8] and acrylonitrile with indoles[9] and imidazoles.[10]

Fluorescent exciplex formation between furan and 1-cyanonaphthalene[8] and between acrylonitrile and 1,2-dimethylindole[9] has been reported. In all these examples the heterocyclic compound is acting as an electron donor. Other reactions have been reported in which heterocyclic compounds such as benzo[*b*]thiophen,[11] isothiazoles,[12] purines,[13a] and pyrimidines[13b] act as electron acceptors. In all these reactions amines were used as donors.

We report upon the formation of fluorescent exciplexes between a variety of heterocyclic compounds and substituted aromatic hydrocarbons and amines.[14] In pertinent cases rate constants for fluorescence quenching were determined.

TABLE 1

Wavelengths of maximum emission for exciplexes formed between heterocyclic compounds and substituted aromatic hydrocarbons in various solvents

Hydrocarbon [E_A^{red} *versus* s.c.e. (V)]	Heterocyclic compound Ionisation potential (eV)]	λ/nm						
		n-Hexane	Cyclohexane	Benzene	Chloroform	Dichloromethane	Ethyl acetate	Acetonitrile
Naphthalene [−2.58]	1,2,5-Trimethylpyrrole	395		412			445	
1-Cyanonaphthalene [−2.00]	2-Methylfuran [8.63]		380	400	412	416	432	
	2,5-Dimethylfuran [8.01]		405	417	441	445	454	
	2,5-Dimethylthiophen [8.18]		382	406		425	423	
	1-Methylpyrrole [8.2]		412	437	445	457		
	1,2,5-Trimethylpyrrole		470	510	525	530		
	1,3,5-Trimethylpyrazole			380			390	410
	1-Methylindole		420	440	457	474		
	1-Methylbenzimidazole		375	385		393	400	404
	Benzo[*b*]furan			387		395	393	408
Anthracene [−1.96]	1,2,5-Trimethylpyrrole			490				
9-Cyanophenanthrene	2,5-Dimethylfuran [8.01]		390	422	445	437	444	
	1-Methylpyrrole [8.2]		395	437	441	446		
	1,2,5-Trimethylpyrrole			512				
	1-Methylindole		415	440	456	467	469	
Pyrene [−2.10]	1,2,5-Trimethylpyrrole			473				

RESULTS

Furans, thiophens, pyrroles, pyrazole, benzofuran, indoles, and benzimidazoles form fluorescent exciplexes with aromatic hydrocarbons (Figure 1). The wavelengths* of the exciplex emissions are given in Table 1. In all cases change from a non-polar to a polar solvent causes a red shift in the emission band indicating that the excited state has charge transfer character. In many cases, change to a highly polar solvent, such as acetonitrile leads to the non-appearance of exciplex emission. A similar observation has been made for other systems exhibiting exciplex formation, *e.g.* aromatic hydrocarbon–amine systems. In those cases where emission is observed in acetonitrile, the solvent effect upon the emission band is far less than for

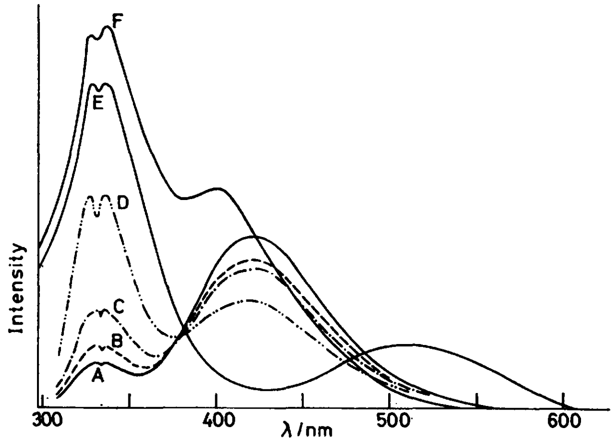

FIGURE 1 Fluorescent spectra for solutions of 1-cyanonaphthalene and (a) 2,5-dimethylfuran (A 8×10^{-2}, B 5×10^{-2}, C 3×10^{-2}, and D 1×10^{-2}M, benzene as solvent); (b) 1,2,5-trimethylpyrrole (E, benzene as solvent); and (c) 1-methylbenzimidazole (F, acetonitrile as solvent)

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* Some of the values differ from those reported in our original communication.[14] This is due to wavelength calibration error on the instrument previously used.

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[7] J. J. McCullough, W. S. Wu, and C. W. Huang, *J.C.S. Perkin II*, 1972, 370.

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[9] K. Yamasaki, T. Matsuura, and I. Saito, *J.C.S. Chem. Comm.*, 1974, 944; *Tetrahedron Letters*, 1975, 313.

[10] Y. Ito and T. Matsuura, *Tetrahedron Letters*, 1974, 513.

[11] P. Grandclaudon, A. Lablache-Combier, and C. Parkanyi, *Tetrahedron*, 1973, **29**, 651.

[12] A. Lablache-Combier and A. Pollet, *Tetrahedron*, 1972, **28**, 3141.

[13] (*a*) N. C. Yang, L. S. Gorelic, and B. Kim, *Photochem. and Photobiol.*, 1971, **13**, 275; A. Stankunas, I. Rosenthal, and J. N. Pitts, *Tetrahedron Letters*, 1971, 4779; (*b*) J.-L. Fourrey and J. Moron, *Tetrahedron Letters*, 1976, 301.

[14] Preliminary communication, R. S. Davidson, A. Lewis, and T. D. Whelan, *J.C.S. Chem. Comm.*, 1975, 203.

those systems in which the emission is quenched in acetonitrile. From the solvent effects upon the emission bands, the dipole moments of the exciplexes were determined and the values obtained are shown in Table 2. These were calculated by plotting the frequency at which the exciplex band occurs in a particular solvent against the frequency at which the anthracene–*NN*-diethylaniline exciplex fluoresces.[15] From the slope of the lines of these plots (see Figure 2) values of $2\mu_c^2/hca^3 = 8.3 \times 10^3$ for the anthracene–*NN*-diethylaniline complex [15] where h = Planck's constant, c = speed of light, and a = cavity of radius of exciplex (taken as 5 Å) could be obtained and from these the dipole moments (μ_c) calculated.

TABLE 2

Dipole moments of exciplexes formed between heterocyclic compounds and aromatic hydrocarbons

Hydrocarbon	Heterocyclic compound	$^2\mu_c^2/hca^3$	Dipole moment μ_c/D [a]
Naphthalene	1,2,5-Trimethylpyrrole	10.96	11.7
1-Cyanonaphthalene	2-Methylfuran	9.96	11.1
	2,5-Dimethylfuran	9.71	11.0
	1-Methylpyrrole	8.47	10.25
	1,2,5-Trimethylpyrrole	8.80	10.45
	1,3,5-Trimethylpyrazole	7.45	9.6
	1-Methylindole	9.96	11.1
	1-Methylbenzimidazole	5.22	8.05
	Benzo[*b*]furan	4.93	7.82
9-Cyanophenanthrene	2,5-Dimethylfuran	10.8	11.6
	1-Methylpyrrole	10.1	11.2
	1-Methylindole	10.2	11.2

[a] Calculated using a cavity radius of 5 Å. Using this value, the dipole moment of the *NN*-diethylaniline–anthracene exciplex is 10.15 D.

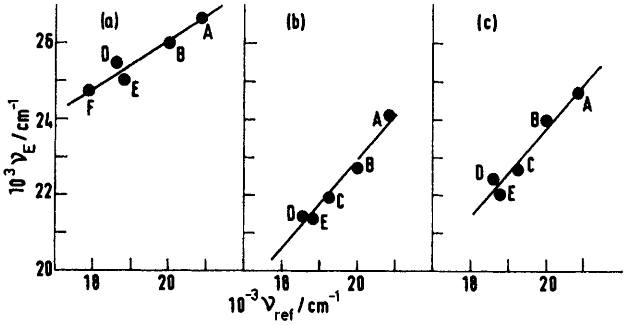

FIGURE 2 Plots of the frequency of the exciplex band for (a) 1-methylbenzimidazole–1-cyanonaphthalene, (b) 1-methylindole–9-cyanophenanthrene, and (c) 2,5-dimethylfuran–1-cyanonaphthalene exciplexes *versus* the frequency of the exciplex band for the anthracene–*NN*-diethylaniline system. Solvents: A = cyclohexane, B = benzene, C = chloroform, D = dichloromethane, E = ethyl acetate, F = acetonitrile

Enthalpies of formation of three exciplexes, 1-cyanonaphthalene–2-methylfuran, 1-cyanonaphthalene–1-methyl pyrrole, and 9-cyanophenanthrene–1-methylpyrrole were determined from a study of the effect of temperature upon the exciplex and monomer emission. Calculations were made according to the method of Birks *et al.*[16] Plots of $\log_e (I_E/I_m[Q])$ *versus* $1/T$ where I_E = intensity of exciplex emission, I_m = intensity of monomer emission, T = temperature, and Q = quencher concentration were made (see Figure 3) and calculations carried out in the prescribed manner. The plots showed two linear regions and $-\Delta H^*$ was calculated from the high temperature portion and energies of activation for exciplex formation calculated from the low temperature portion. The results are given in Table 3.

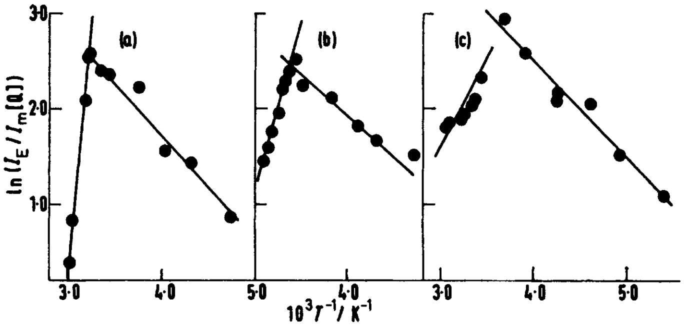

FIGURE 3 Plots of the intensities of the exciplex *versus* monomer bands as a function of temperature for (a) 9-cyanophenanthrene–1-methylpyrrole, (b) 1-cyanonaphthalene–2-methylfuran, and (c) 1-cyanonaphthalene–1-methylpyrrole

TABLE 3

Enthalpies of formation ($-\Delta H^*$) and energies of activation (E_a) for formation of exciplexes between aromatic hydrocarbons and heterocyclic compounds (toluene as solvent)

Exciplex	$-\Delta H^*$/ kcal mol^{-1}	E_a/ kcal mol^{-1}
1-Cyanonaphthalene-2-methylfuran	4.6	1.5
1-Cyanonaphthalene–1-methylpyrrole	11.5	3.5
9-Cyanophenanthrene–1-methylpyrrole	7.1	1.0

Addition of 2-methylfuran, 2,5-dimethylfuran, benzo[*b*]furan, and 1-methylbenzimidazole to solutions of 1-cyanonaphthalene led to quenching of the cyanonaphthalene fluorescence and in some solvents the appearance of an exciplex band (see Table 1). When exciplex emission was observed an isoemissive point was obtained. This was not the case when pyrroles and indoles were used. These compounds act as quenchers for the exciplex emission and this probably involves the formation of a termolecular species. In none of the cases we examined was emission observed which could be attributed to such a species.

In the case of pyrroles and indoles, fluorescent exciplexes could not be observed unless the nitrogen atom was alkylated. This parallels the observation in the hydrocarbon–amine systems in which fluorescent exciplexes are only observed with tertiary aliphatic and aromatic amines.[1,3] The high chemical reactivity of the N–H bonds in pyrroles and indoles probably gives rise to an efficient non-radiative decay process for the encounter complexes formed by these compounds.

Several examples were found in which heterocyclic compounds quenched the fluorescence of polycyclic aromatic hydrocarbons but did not produce a fluorescent exciplex. Quenching rate constants for these systems and some of those described in Table 1 have been measured and are recorded in Table 4. The rate constants for quenching the fluorescence of benzenoid compounds by heterocycles has been previously reported.[17]

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[15] H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, 1967, **47**, 1183.

[16] J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. Roy. Soc.*, 1964, *A*, **280**, 289.

[17] M. E. Sime, D. Phillips, and K. Al-Ani, *Mol. Photochem.*, 1976, **7**, 149.

Quenching of the fluorescence of 2,5-diphenyl-1,3,4-oxadiazole and 2,4,5-triphenyloxazole by amines has been examined and Stern–Volmer quenching constants are given in Table 5. In some cases fluorescent exciplexes were observed.

TABLE 4

Rate constants for the quenching of fluorescence from aromatic hydrocarbons by heterocyclic compounds

Aromatic hydrocarbon [$E_A^{\text{red.}}$ *versus* s.c.e. (V)]	Heterocyclic compound [Ionisation potential (eV)]	Solvent	Quenching rate constant ($\text{l mol}^{-1}\text{ s}^{-1}$)
Anthracene [−1.96]	1-Methylpyrrole [8.2]	A	0.82×10^9
1-Cyanonaphthalene [−2.00]	Furan [8.89]	A	1.0×10^9
	Furan [8.89]	C	0.04×10^9
	2,5-Dimethylthiophen [8.18]	A	10.7×10^9
	1,2,5-Trimethyl-pyrrole	A	13.6×10^9
	Benzo[*b*]furan	A	7.0×10^9
	Benzo[*b*]thiophen	A	8.5×10^9
	1-Methyl-benzimidazole	A	6×10^9
	2-Methylbenzoxazole	B	0.44×10^9
	2-Methylbenzoxazole	A	0.2×10^9
	1-Methyl-benzotriazole	B	1.3×10^9
	1-Methyl-benzotriazole	A	1.2×10^9
9-Cyanoanthracene	Furan [8.89]	A	0.01×10^9
	Furan [8.89]	C	0.01×10^9
	Thiophen [8.87]	C	0.01×10^9
	Thiophen [8.87]	A	0.01×10^9
	2,5-Dimethylfuran [8.01]	A	5×10^9
	2,5-Dimethylfuran [8.01]	C	3×10^9
	1-Methylpyrrole [8.2]	A	6.5×10^9
	1-Methylpyrrole [8.2]	C	2×10^9

A = Acetonitrile, B = benzene, C = cyclohexane.

TABLE 5

Stern–Volmer rate constants (l mol^{-1}) for the quenching of the fluorescence of heterocyclic compounds by amines in benzene solution

	Triethylamine	1,2,5-Tri-methylpyrrole
2,4,5-Triphenyloxazole [a]	5.5	20.2
2,5-Diphenyl-1,3,4-oxadiazole [b]	33	38.4

[a] Forms a fluorescent exciplex ($\lambda_{\text{max.}}$ 448 nm) with *NN*-dimethylaniline in benzene solution and one with 1,2,5-trimethylpyrrole ($\lambda_{\text{max.}}$ 460 nm) in benzene. [b] Forms a weak fluorescent ($\lambda_{\text{max.}}$ 488 nm) exciplex with 1,2,5-trimethylpyrrole in benzene.

DISCUSSION

From the results shown in Table 1 it can be clearly seen that many heterocyclic compounds quench the fluorescence of aromatic hydrocarbons and that in many cases fluorescent exciplexes are formed. Since in none of the systems could association between the hydrocarbon and heterocycle be detected by u.v. spectroscopy, the quenching is attributed to a diffusional quenching process. The observation in many of the systems of an isoemissive wavelength indicates that only two molecules are involved in the quenching. The values of the dipole moments given in Table 2 show that many of the exciplexes have considerable charge transfer character. It is particularly significant that in the three cases where emission is observed in acetonitrile, that the exciplex has less charge-transfer character than the anthracene–*NN*-diethylaniline exciplex. This probably reflects the lower favourability for radical ion formation in these systems. In many cases, formation of such species provides an efficient non-radiative pathway for the encounter complex.

From Table 3 it can be seen that the exciplex formed between 1-cyanonaphthalene and 1-methylpyrrole is more stable than that formed between 1-cyanonaphthalene and 2-methylfuran. The lower stability of the exciplex derived from 2-methylfuran is to be expected from the fact that the ionisation potential of this heterocycle (8.39 eV) is higher than that of 1-methylpyrrole.[14] From the finding that the exciplex formed between 1-methylpyrrole and 9-cyanophenanthrene is less stable than that formed between the heterocycle and 1-cyanonaphthalene it would appear that the cyanophenanthrene is a poorer electron acceptor than 1-cyanonaphthalene. Unfortunately there are no details of the reduction potentials of these compounds.

The values for the energies of activation for the complexes are similar to those for many other exciplex systems. It is surprising to see that the energy of activation is higher for exciplex formation between 1-cyanonaphthalene and 1-methylpyrrole than for the exciplex involving 2-methylfuran. The ground state repulsive energies in the two systems [calculated from $\delta E_{\text{rep.}} = E_{00} - (\Delta H + h\nu^{\text{max}})$ where E_{00} = energy of 0–0 transition of the fluorescor and $h\nu_{\text{max.}}$ = energy of the $\lambda_{\text{max.}}$ of fluorescence for the exciplex] are *ca.* 5 kcal mol^{-1}, *i.e.* very similar to the values for exciplexes involving aromatic amines. One can only conclude that the difference in the position of substitution in the heterocycles gives rise to steric effects which are different for the two compounds and in the case of the pyrrole, these are sufficiently large to over-ride its advantage over the furan in having a lower ionisation potential.

From the quenching rate constants given in Table 4 it can be seen that the rate constant increases as the ionisation potential of the donor decreases, *e.g.* 9-cyanoanthracene fluorescence is more efficiently quenched by 2,5-dimethylfuran than by furan. Exciplex formation and the quenching of the hydrocarbon fluorescence is also facilitated by the hydrocarbon bearing an electron-withdrawing group, *e.g.* the quenching of anthracene fluorescence by 1-methylpyrrole is less efficient than that for 9-cyanoanthracene. Furthermore a fluorescent exciplex involving naphthalene could be observed with 1,2,5-trimethylpyrrole but not with furans whereas 1-cyanonaphthalene formed fluorescent exciplexes with these heterocycles.

It will be noted that for some of the systems reported in Table 4 that the rate constant for quenching increases on change of solvent from cyclohexane to acetonitrile. In the more polar solvent there is the possibility that the quenching complex gives radical ions and consequently, the reaction to regenerate the excited singlet state of the hydrocarbon and the ground state heterocycle is suppressed. Suppression of k_{-1} will cause an increase in K.

$$\mathrm{ArH}_{\mathrm{S_1}}{}^{*} + \mathrm{Het.} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{ArHHet})^{*} \longrightarrow \text{Radical ions}$$

$$\text{Quenching constant } K = k_1/k_{-1}$$

In those cases where there is a lack of a solvent effect upon the quenching constant there is the possibility that either (a) the system cannot yield radical ions, even in polar solvents or (b) the quenching complex never breaks up to give the excited singlet state of the hydrocarbon and the ground state of the heterocycle.

In all the foregoing examples the heterocyclic compound is acting as an electron donor. For the examples shown in Table 5 they are acting as acceptors. The greater efficiency of quenching by the trimethylpyrrole compared with triethylamine is probably a reflection of its lower ionisation potential.

EXPERIMENTAL

Materials.—Before use, materials were subjected to purification procedures until their m.p.s or b.p.s accorded with literature values. 9-Cyanophenanthrene, 9-cyanoanthracene, 1-methylindole, 2,5-diphenyl-1,3,4-oxadiazole, and 2,4,5-triphenyloxazole were purified by recrystallisation. 1-Methylindole was distilled under nitrogen prior to use. 1,2,5-Trimethylpyrrole, benzo[*b*]furan, benzo[*b*]thiophen, and *NN*-dimethylaniline were distilled *in vacuo*. Furan, thiophen, 2-methylfuran, and 2,5-dimethylfuran were dried and freed from peroxides by treatment with lithium aluminium hydride followed by distillation.

All solvents were Merck Uvasol spectrograde solvents.

Spectrofluorimetry.—Measurements were made on Baird Atomic SF100E and Perkin-Elmer MPF4 instruments. Wavelengths measurements are accurate to within ±2 nm and intensity measurements are within ±2%. For variable temperature runs, the degassed sample was contained in a cylindrical quartz tube of internal diameter 2 mm. This was cooled by a stream of pre-cooled, dry nitrogen gas. Temperatures could be maintained to ±1°. Lifetime measurements were made on an Applied Photophysics pulse sampling fluorimeter.

We thank the S.R.C. for maintenance grants (to A. L. and T. D. W.) and for funds to purchase the spectrofluorimeters, and the Royal Society for funds to purchase the lifetime apparatus.

[6/1815 *Received, 27th September*, 1976]