Naphthalene Photocatalysed Decomposition of Chlorobenzenes in Exciplex Forming Systems

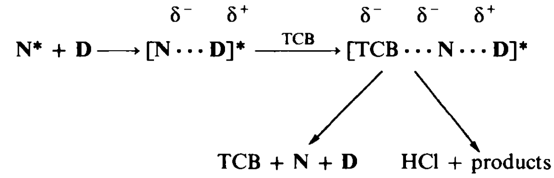
Carlos A. Chesta,* Vicente Avila, Arnaldo T. Soltermann, Carlos M. Previtali and Juan J. Cosa*
Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina

The photophysical behaviour of *N,N*-diethyl-2-(1-naphthyl)ethylamine **I**, *N*-benzyl-*N*-ethyl-2-(1-naphthyl)ethylamine **VI** and *N*-ethyl-2-(1-naphthyl)-*N*-(2,4,6-trichlorobenzyl)ethylamine **VII**, molecules that are able to form intramolecular exciplexes, has been examined in ethyl acetate. Compounds **I** and **VI** are fluorescent, but **VII** is non fluorescent and decomposes with formation of hydrogen chloride. The behaviour of the intermolecular exciplexes formed by naphthalene **N** and the bifunctional quenchers *N,N*-diethylbenzylamine **II**, 4-chloro-*N,N*-diethylbenzylamine **III**, 3,5-dichloro-*N,N*-diethylbenzylamine **IV** and 2,4,6-trichloro-*N,N*-diethylbenzylamine **V** has also been studied.

The photodechlorination quantum yields have been determined for the systems **I** + trichlorobenzene, **N** + **V** and **VII** and compared with that of the system **N** + triethylamine + trichlorobenzene. The production of hydrogen chloride in these reactions is explained by an electron transfer model in which the naphthalene behaves as a photocatalyst. Evidence is given for the quenching of exciplexes formed by naphthalene and an amine, by the electron acceptor trichlorobenzene, occurring from the acceptor (naphthalene) side of the exciplex.

The photodechlorination of chlorinated aromatic compounds is a topic of current interest because of the importance of some chlorinated compounds as environmental pollutants. Among the methods employed to dechlorinate aromatic compounds, a photosensitized route employing aliphatic[1–3] and aromatic amines[4–7] has received attention during recent years. These reactions proceed by an electron transfer mechanism where the amine is the electron donor and the chloroaromatic compound the electron acceptor. The uptake of the electron by the chlorinated compound is followed by the decomposition of the radical anion into a chloride ion and an aromatic radical. When these studies have been carried out in low polarity solvents, exciplexes have been reported as intermediates.[8–10]

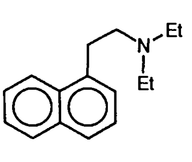
We have reported that the fluorescence of the exciplex formed between naphthalene (N) and triethylamine (TEA) is quenched by chlorobenzenes.[11] The quenching of exciplexes by a third molecule has been the subject of several studies.[12] It has been proposed that the quenching mechanism involves the formation of an excited termolecular complex or terplex. In most cases the terplex decays to the ground state by non-radiative pathways. In some cases the emission from the terplex or an exciplex substitution product is observed;[12–14] in a very few cases chemical reactions have been attributed to exciplex quenching.[12,15] In solvents of intermediate polarity such as ethyl acetate, the quenching of the N–TEA exciplex by trichlorobenzene (TCB) is accompanied by the production of hydrogen chloride, clear evidence of the effective reduction of the chloroaromatic compound. In the mechanism proposed to explain the above experimental results, the naphthalene behaves as a photocatalyst and the exciplex transfers an electron to the chlorobenzenes. To explain the results of the N–TEA–TCB system it was assumed that the fluorescence quenching of the exciplex by TCB produces a terplex intermediate, which can either decompose yielding HCl or undergo back electron transfer to the ground state, Scheme 1. The net result is the photoinduced transfer of one electron from TEA to the chlorobenzene without excitation of either partner. For the sake of comprehensibility in all the schemes the amine donor is represented by **D**.



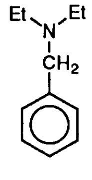
Scheme 1

As proposed by Beens and Weller[13] and confirmed by Caldwell *et al.*[12] exciplex quenching by electron donors should occur from the donor (amine) side while quenching by electron acceptors should occur from the acceptor (naphthalene) side of the exciplex. Since exciplexes are expected to be relatively structured, one of the 'faces' of naphthalene in the exciplex N–TEA must be shielded by the amine residue. The attack of the chloroaromatic electron acceptor quencher should then occur at the opposite side of the naphthalene. Hence, it may be concluded that the quenching process should be subject to some geometrical restrictions.

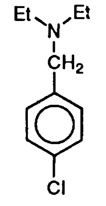
To investigate how structural factors affect the efficiency of the photocatalytic decomposition of chlorobenzenes, we have synthesized several compounds (**I–VII**) in which two or three of the molecules taking part in the electron transfer process shown in Scheme 1 are linked by flexible covalent bonds. Different dechlorination efficiencies should be expected if the chloroaromatic compound is compelled to remain on the opposite side of the naphthalene ring in the terplex. Therefore, we have prepared several aromatic amines with different chlorine substitution patterns on the ring (structures **II–V**). When these molecules interact with singlet excited naphthalene and the exciplex is formed, the chloroaromatic moiety may be precluded from approaching the naphthalene ring from the same side as the amine. Consequently the dechlorination process may be expected to be less efficient. A similar effect may occur in structure **VII** where all three members of the exciplex are covalently linked. Compound **VI** was prepared as a reference molecule for the properties of an exciplex not having chlorine



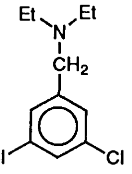
I



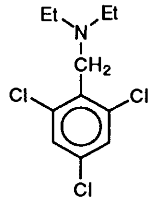
II



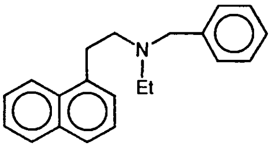
III



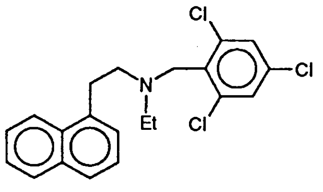
IV



V



VI



VII

substitution. Compound **I** is an intramolecular version of the exciplex shown in Scheme 1 and it was included for comparison with the intermolecular system. The photophysical behaviour of the exciplexes formed from naphthalene with **II**–**V** and of molecules **VI** and **VII** has been examined in ethyl acetate. The photodechlorination quantum yields were determined for **I**–TCB, N–**V** and **VII** systems. These were chosen because they contain the same components as the original non-linked system. The dechlorination results for the N–**V** and **VII** systems support the model that exciplex quenching by electron acceptors occurs from the acceptor (naphthalene) side of the exciplex.

Experimental

Naphthalene (Aldrich 99%) was sublimed twice before use. Triethylamine (TEA; Carlo Erba) was RPE grade and was vacuum distilled before use. Ethyl acetate and cyclohexane of spectroscopic grade were obtained from Sintorgan and used as received. All the starting materials used in the synthesis of amines **I**–**VII** were obtained from Aldrich.

Preparation of the Amines **I**–**VII**.—The amines, *N*,*N*-diethyl-2-(1-naphthyl)ethylamine **I**, *N*-benzyl-*N*-ethyl-2-(1-naphthyl)-ethylamine **VI** and *N*-ethyl-2-(1-naphthyl)-*N*-(2,4,6-trichlorobenzyl)ethylamine **VII**, and the bifunctional quenchers that also have an amine group, *N*,*N*-diethylbenzylamine **II**, 4-chloro-*N*,*N*-diethylbenzylamine **III**, 3,5-dichloro-*N*,*N*-diethylbenzylamine **IV** and 2,4,6-trichloro-*N*,*N*-diethylbenzylamine **V**, were prepared by $LiAlH_4$ reduction of the corresponding amide, which was obtained from the appropriate acid chloride and amine.[16,17] The *N*-(2,4,6-trichlorobenzyl)ethylamine, required for the synthesis of amine **VII**, was prepared by reduction of the imine. The imine was obtained from the condensation reaction between 2,4,6-trichlorobenzaldehyde and *N*-ethylamine.[18]

N,N-*Diethyl*-2-(1-*naphthyl*)*ethylamine* **I**. $\delta_H(CDCl_3)$ 1.15 (t, 6 H, CH_3), 2.75 (q, 4 H, CH_2CH_3), 2.90 (t, 2 H, $ArCH_2CH_2$), 3.27 (t, 2 H, $ArCH_2$), 7.25–8.10 (m, 7 H, ArH). The mass spectrum showed a weak molecular ion peak at *m*/*z* 227 (Found: C, 84.4; H, 9.3; N, 6.2. Calc. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16%).

N,N-*Diethylbenzylamine* **II**. $\delta_H(CDCl_3)$ 1.05 (t, 6 H, CH_3), 2.5 (q, 4 H, CH_2), 3.5 (s, 2 H, $PhCH_2$), 7.3 (s, 5 H, ArH). The mass spectrum showed a weak molecular ion peak at *m*/*z* 163 (Found: C, 80.7; H, 10.5; N, 8.4. Calc. for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58%).

4-*Chloro*-N,N-*diethylbenzylamine* **III**. $\delta_H(CDCl_3)$ 1.05 (t, 6 H, CH_3), 2.5 (q, 4 H, CH_2), 3.5 (s, 2 H, $PhCH_2$), 7.25 (s, 4 H, ArH). The mass spectrum showed weak peaks at *m*/*z* 197 (M) and 199 (M + 2) as expected for a chloroaromatic compound (Found: C, 66.6; H, 8.1; N, 7.0. Calc. for $C_{11}H_{16}ClN$: C, 66.83; H, 8.16; N, 7.08; Cl, 17.93%).

3,5-*Dichloro*-N,N-*diethylbenzylamine* **IV**. $\delta_H(CDCl_3)$ 1.05 (t, 6 H, CH_3), 2.5 (q, 4 H, CH_2), 3.5 (s, 2 H, $PhCH_2$), 7.1–7.3 (m, 3 H, ArH). The mass spectrum showed weak peaks at *m*/*z* 231 (M) and 233 (M + 2) (Found: C, 56.7; H, 6.5; N, 5.8. Calc. for $C_{11}H_{15}Cl_2N$: C, 56.91; H, 6.51; N, 6.03; Cl, 30.54%).

2,4,6-*Trichloro*-N,N-*diethylbenzylamine* **V**. $\delta_H(CDCl_3)$ 1.05 (t, 6 H, CH_3), 2.5 (q, 4 H, CH_2), 3.5 (s, 2 H, $PhCH_2$), 7.3 (s, 2 H, ArH). The mass spectrum obtained is very complex but it showed a peak at *m*/*z* 265 (M), which corresponds to the molecular ion peak (Found: C, 49.3; H, 5.2; N, 5.3. Calc. for $C_{11}H_{14}Cl_3N$: C, 49.56; H, 5.29; N, 5.25; Cl, 39.89%).

N-*Benzyl*-N-*ethyl*-2-(1-*naphthyl*)*ethylamine* **VI**. $\delta_H(CDCl_3)$ 1.2 (t, 3 H, CH_3), 2.75 (q, 2 H, CH_2CH_3), 2.90 (t, 2 H, $NaphthCH_2CH_2$), 3.27 (t, 2 H, $NaphthCH_2$), 3.80 (s, 2 H, $PhCH_2$), 7.25–8.10 (m, 12 H, ArH). The mass spectrum showed a weak molecular ion peak at *m*/*z* 289 (Found: 87.0; H, 8.1; N, 4.75. Calc. for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84%).

N-*Ethyl*-2-(1-*naphthyl*)-N-(2,4,6-*trichlorobenzyl*)*ethylamine* **VII**. $\delta_H(CDCl_3)$ 1.2 (t, 3 H, CH_3), 2.75 (q, 2 H, CH_2CH_3), 2.90 (t, 2 H, $NaphthCH_2CH_2$), 3.27 (t, 2 H, $NaphthCH_2$), 3.80 (s, 2 H, $PhCH_2$), 7.25–8.10 (m, 9 H, ArH). The mass spectrum is very complex showing a molecular ion peak at *m*/*z* 391 (Found: C, 64.1; H, 5.1; N, 2.81. Calc. for $C_{21}H_{20}Cl_3N$: C, 64.22; H, 5.13; N, 3.53; Cl, 27.08%).

Data Collection.—NMR spectra were taken on a General Electric 300 MHz NMR spectrometer. Mass spectra were obtained using a Hewlett Packard HP 5980 A gas chromatograph with a HP 5972 mass detector. Solutions were photolysed at 310 nm by means of a PTI arc lamp monochromator system. Light intensity was measured using azobenzene as actinometer.[19,20] Chloride ion measurements were performed with an ion selective electrode as previously described.[6] The conversion of the different chlorobenzenes was always kept below 10%. All the solutions were deaerated by nitrogen bubbling.

Fluorescence measurements were carried out with an Aminco Bowman spectrofluorometer. Fluorescence quantum yields were obtained with quinine bisulfate as fluorescence standard. Fluorescence lifetime measurements were taken with an arc lamp (Xenon nanolamp, 10 ns FWHM) as the excitation source. The sample was located in the cavity of a TRW 75-A filters fluorometer. The signal of the photomultiplier was displayed, averaged and digitized by a Hewlett Packard 54200A oscilloscope. It was then transferred through an IEEE interface to a PC computer where it was processed. The estimated error was ±4% or ±0.5 ns whichever is the greater.

Results

Amine **I**–1,3,5-*Trichlorobenzene* (*TCB*).—When naphthalene and TEA are linked by a methylene chain, it has been reported that after excitation of the naphthalene moiety it is possible to observe intramolecular exciplex formation.[21–24] The photophysics of intramolecular exciplexes similar to **I** (where the substituents on the amine nitrogen were methyl instead of ethyl) have been extensively studied.[25–27] Irreversible exciplex formation was observed in solvents such as 2-methyltetra-

Table 1 Photophysical parameters of the exciplexes in ethyl acetate

Exciplex	λ_{max}/nm	φ_f	τ/ns
I	440	0.105	14.5 ± 0.5
N–TEA	475	0.0045	15.0 ± 0.5
N–**II**	455	0.0061	15.6 ± 0.6
N–**III**	450	0.0061	18.9 ± 0.8
N–**IV**	450	0.0012	14.8 ± 0.5
N–**V**	450	0.0006	11.3 ± 0.5(17.0 ± 1.0)
VI	425	0.133	11.3 ± 0.5
VII	n.o.[a]	n.o.	n.o.

[a] n.o. = not observed.

Table 2 Bimolecular rate constants k_q for the different systems that involve quenching of a naphthalene–amine exciplex by a TCB residue and efficiency η_r for HCl formation

System	k_q/dm^3 mol^{-1} s^{-1}	η_r
N–TEA/TCB	5.0×10^8	0.050 ± 0.008
I/TCB	7.7×10^8	0.035 ± 0.004
N–**V**	n.o.[a]	—
N–**V**/**V**	2.8×10^8	0.020 ± 0.002
VII	—	0.030 ± 0.004

[a] n.o. = not observed.

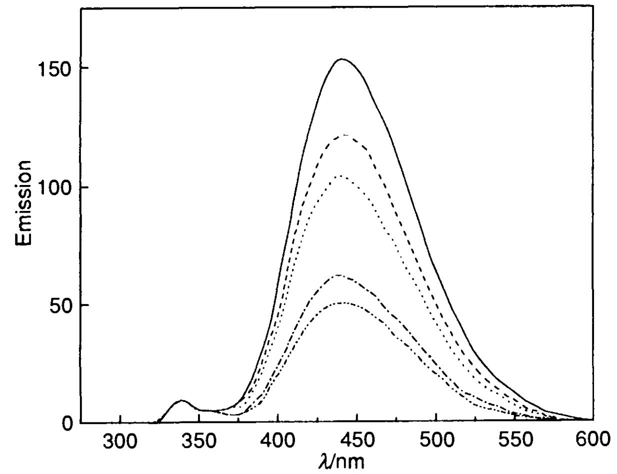


Fig. 1 Fluorescence spectra and fluorescence quenching of **I** by 1,3,5-trichlorobenzene: —— [TCB] = 0; ---- [TCB] = 0.025 mol dm^{-3}; ···· [TCB] = 0.047 mol dm^{-3}; —·—·— [TCB] = 0.139 mol dm^{-3}; —··—··— [TCB] = 0.182 mol dm^{-3}

hydrofuran, diethyl ether and butyl acetate. In contrast to intermolecular exciplexes of aromatic hydrocarbons and amines, the intramolecular exciplex of **I** fluoresces in polar solvents such as acetonitrile.[22-24] However, to make the results comparable with those of the intermolecular N–TEA exciplex[11] the experiments were carried out in ethyl acetate.

The absorption spectrum of compound **I** in ethyl acetate is similar to that of 1-ethylnaphthalene. Upon excitation of the naphthalene chromophore, **I** shows two fluorescence bands. One of them corresponds to a weak residual fluorescence of the naphthalene moiety and the other is an intense red shifted band assignable to the intramolecular exciplex. The fluorescence quantum yield (φ_f), the decay time (τ_e) and the maximum emission wavelengths of this exciplex are summarized in Table 1. Table 1 also includes, for the sake of comparison, the corresponding parameters for the N–TEA intermolecular exciplex.

The fluorescence of the intramolecular exciplex of **I** is quenched by the addition of 1,3,5-trichlorobenzene (Fig. 1). The quenching rate constant k_q, was measured by static and time resolved techniques, giving a value of $7.7 \pm 0.5 \times 10^8$ dm^3 mol^{-1} s^{-1} that is very close to that observed for the N–TEA system, 5.0×10^8 dm^3 mol^{-1} s^{-1}.

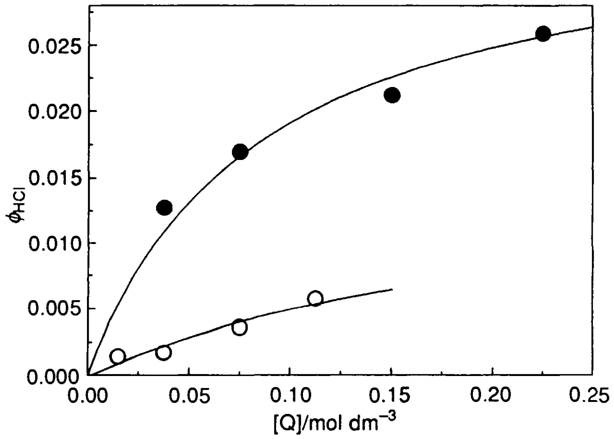
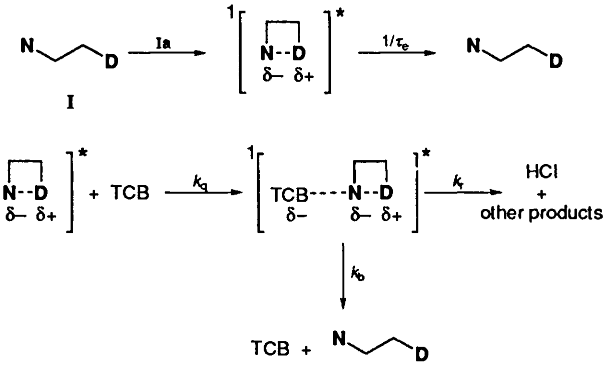


Fig. 2 Hydrogen chloride quantum yield as a function of quencher concentration [Q] for different systems: (●) **I**–TCB; (○) N–**V**

The irradiation of compound **I** at 310 nm in the presence of TCB leads to the formation of HCl with photoreduction of the chloroaromatic compound. The quantum yield of hydrogen chloride formation as a function of the TCB concentration is shown in Fig. 2. The experimental results are interpreted with the following simplified mechanism, Scheme 2. It is assumed that the same electron transfer mechanism operates as that previously proposed for the quenching of the intermolecular N–TEA exciplex by TCB (Scheme 1).



Scheme 2

A steady-state analysis of Scheme 2 gives eqn. (1), where η_r =

$$\varphi_{HCl} = \eta_r\{(k_q\tau_e[TCB])/(1 + k_q\tau_e[TCB])\} \quad (1)$$

$k_r/(k_r + k_b)$ is the efficiency of the terplex intermediate to produce HCl.

The experimental HCl quantum yields presented in Fig. 2, as a function of the TCB concentration, can be fitted by a non-linear least-squares analysis of eqn. (1) with the efficiency η_r as an adjustable parameter. The η_r values for all the systems studied are collected in Table 2.

Naphthalene with Amines **II**, **III**, **IV** *and* **V**.—The quenching of excited singlet state naphthalene by the benzylamines **II**–**V** is independent of the chloro substitution on the ring. Fig. 3 shows a Stern–Volmer plot for the four amines, the plot is linear over a large range of concentrations. The quenching rate constant obtained was 3×10^9 dm^3 mol^{-1} s^{-1} for the four amines studied. This rate constant is very similar to that observed for

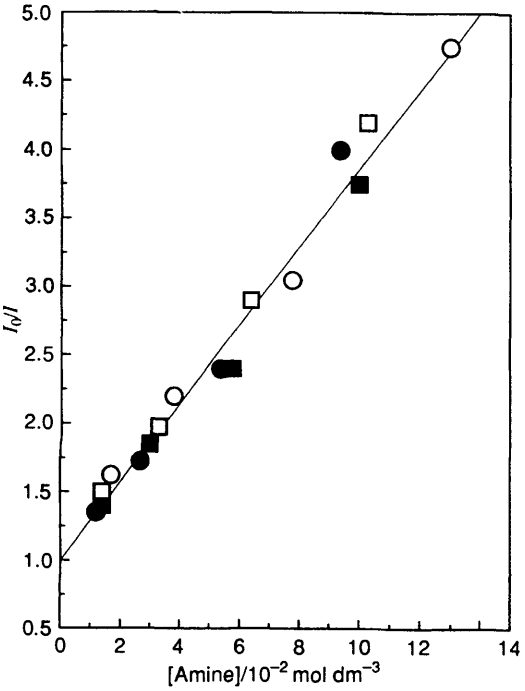


Fig. 3 Stern–Volmer plot for the fluorescence quenching of naphthalene by the bifunctional quenchers II–V: (●) II; (□) III; (○) IV; (■) V

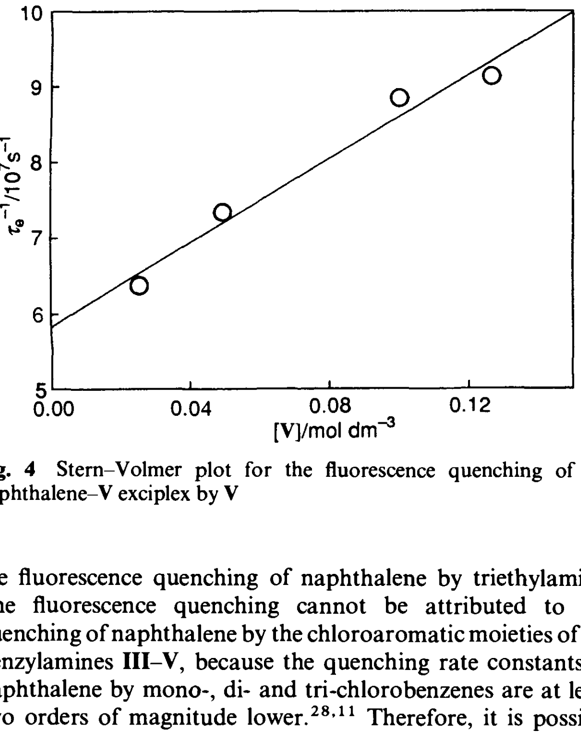
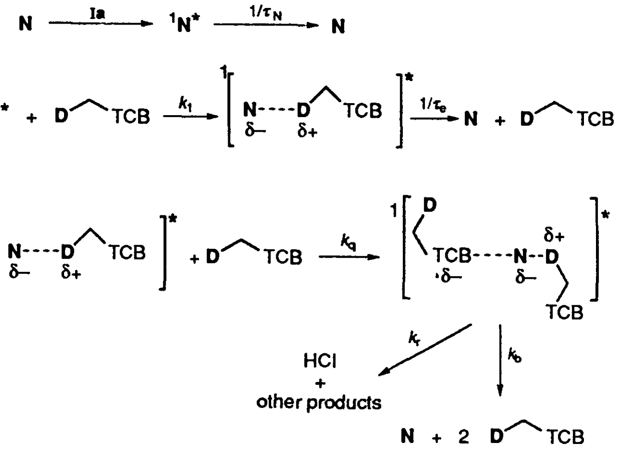


Fig. 4 Stern–Volmer plot for the fluorescence quenching of the naphthalene–V exciplex by V

the fluorescence quenching of naphthalene by triethylamine. The fluorescence quenching cannot be attributed to the quenching of naphthalene by the chloroaromatic moieties of the benzylamines III–V, because the quenching rate constants of naphthalene by mono-, di- and tri-chlorobenzenes are at least two orders of magnitude lower.[28,11] Therefore, it is possible to conclude that the above quenching processes are mainly attributable to the amine group of the quenchers; with the singlet excited state of the naphthalene acting as an electron acceptor and the benzylamines as electron donors. In all cases, the quenching was accompanied by the appearance of a broad red shifted band attributable to the formation of intermolecular exciplexes. The more relevant characteristics of these exciplexes are given in Table 1. The decay times (τ_e) and fluorescence quantum yields (φ_f) of the exciplexes were measured at a benzylamine concentration 0.1 mol dm^{-3}; at this large amine concentration at least 95% of the naphthalene is quenched.

In the case of the N–V exciplex the decay time depends on the concentration of the amine. However, the lifetimes of the exciplexes formed by naphthalene and the amines **II**, **III** and **IV** were independent, within experimental error, of the amine concentration. Fig. 4 shows a plot of $1/\tau_e$ for the **N**–**V** exciplex *versus* the concentration of **V**. From the slope of this plot we obtained a quenching rate constant of 2.8×10^8 dm^3 mol^{-1} s^{-1} and from the intercept a τ_e^0 value of 17.0 ± 1.0 ns. Here τ_e^0 is the fluorescence decay time of the exciplex extrapolated to zero amine concentration. The corresponding fluorescence quantum yield for this exciplex was estimated as 0.0006. The rate constant for the fluorescence quenching of the **N**–**V** exciplex by **V** is very similar to the quenching rate constant of the N–TEA exciplex by TCB.[11] Therefore, we ascribe this quenching to the intermolecular attack of the exciplex by the trichlorobenzyl residue of trichlorobenzylamine **V**.

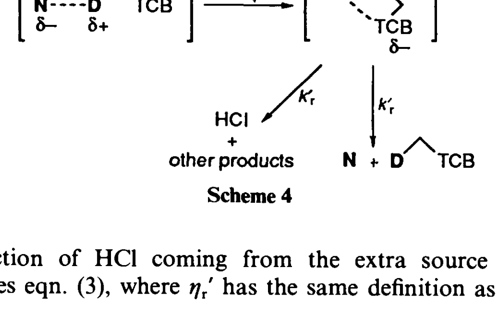
The photolysis of **N** in the presence of **V** leads to the dechlorination of the benzylamine. Fig. 2 shows the experimental quantum yields of HCl as a function of the concentration of **V**. Taking into account the observed quenching of the exciplex by **V** the results can be explained by the mechanism shown in Scheme 3. A steady state analysis gives eqn. (2) for the global quantum yield of hydrogen chloride.



Scheme 3

$$\varphi_{HCl} = \eta_r\{(k_1\tau_N[V])/(1 + k_1\tau_N[V])\} \times \{(k_q\tau_e[V])/(1 + k_q\tau_e[V])\} \quad (2)$$

Fig. 2 also shows the fitting of the experimental results to eqn. (2) taking η_r as an adjustable parameter. The above mechanism only takes into account the transfer of one electron from the intermolecular exciplex **N**–**V** to the chlorinated moiety of another **V** molecule as a possible source of HCl. It neglects the possible production of HCl directly from the **N**–**V** exciplex. If this pathway is considered, the additional pathways shown in Scheme 4 should be added to Scheme 3. Eqn. (2) must be modified to include the eventual



Scheme 4

production of HCl coming from the extra source and it becomes eqn. (3), where η_r' has the same definition as η_r and

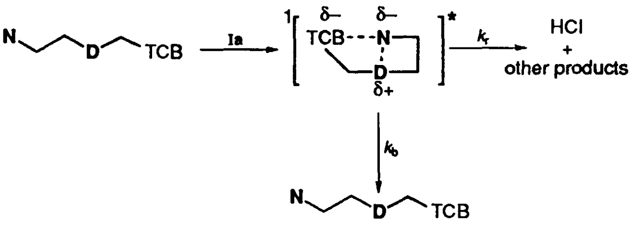
k_q' is the rate constant for an intramolecular electron transfer occurring in the exciplex.

$$\varphi_{HCl} = \eta_r\left(\frac{k_1\tau_N[\mathbf{V}]}{1 + k_1\tau_N[\mathbf{V}]}\right)\left(\frac{k_q\tau_e[\mathbf{V}]}{1 + k_q\tau_e[\mathbf{V}]}\right) + \eta_r' k_q' \tau_e\left(\frac{k_1\tau_N[\mathbf{V}]}{1 + k_1\tau_N[\mathbf{V}]}\right) \quad (3)$$

Fitting the experimental data to eqn. (3) using η_r and the product (η_r', k_q' τ_e) as adjustable parameters gives η_r as 0.019 ± 0.004 for the external quenching and (η_r' k_q' τ_e) as 0.0004 ± 0.0004 for the intramolecular case. The use of eqn. (3) does not produce a significant improvement in the fitting. The value of η_r' k_q' τ_e is small relative to η_r. This may be due to a small η_r' or to a small k_q'. Whatever the reason, the results suggest that the relative importance of the intramolecular pathway is negligible. Therefore we adopted the simplified Scheme 3 as the source of HCl.

Exciplexes **VI** *and* **VII**.—Similarly to compound **I**, compound **VI** shows two fluorescence bands; one corresponding to the residual fluorescence of naphthalene and a red-shifted band assignable to intramolecular exciplex formation. The more relevant characteristics of this exciplex are summarized in Table 1.

Compound **VII** is not fluorescent and it decomposes yielding hydrogen chloride. The lack of fluorescence of **VII** can be ascribed to the proximity of the trichlorobenzyl group to the naphthalene ring. Here there is a fast intramolecular electron transfer from the exciplex to the trichlorobenzyl group followed by its dechlorination. The quantum yield for HCl formation was found to be independent on the concentration of **VII**. These results are resumed in Scheme 5.



Scheme 5

A steady state analysis of Scheme 5 gives eqn. (4) for the quantum yield of hydrogen chloride. Note that eqn. (4) also

$$\varphi_{HCl} = k_r/(k_r + k_b) \quad (4)$$

represents the efficiency η_r of the intermediate terplex to yield products and as such is also included in Table 2.

Discussion

The fluorescence maxima and decay times of the exciplexes formed between naphthalene and the benzylamines **II**–**V** are quite similar (Table 1). This suggests that these exciplexes have similar structures and solvation. However, the fluorescence quantum yields of the exciplexes are dependent on the number of chlorine atoms in the aromatic ring. The fluorescence quantum yields decrease with the number of chlorine atoms. A decrease in the fluorescence quantum yield is associated with a decrease in the decay time, thus making the behaviour of these series of exciplexes truly atypical. The lack of (or very low) intramolecular HCl production from the **N**–**V** exciplex is concordant with the invariance of the decay times of the exciplexes. If intramolecular electron transfer were an important deactivation pathway in these exciplexes, then intramolecular HCl production would be observed and the decay times would depend on the chlorine substitution on the benzylamine donor. The above results may be explained if the chlorobenzylamine group is at such a long distance from the naphthalene radical anion that electron transfer cannot occur. To obtain HCl a second chlorobenzylamine molecule is necessary and this molecule should approach the exciplex on the naphthalene side. In compound **VII** the chloroaromatic moiety must be near the naphthalene ring (see below) and a second molecule is not necessary to form HCl. Therefore, it can be concluded that the species leading to HCl formation is a terplex with conformation **TCB**–**N**–**D**.

It is well known that, if energetically favourable, triplet state formation can occur through intersystem crossing from exciplexes.[29–31] Then, spin–orbit coupling between the exciplex and the locally excited triplet state should be enhanced by substituting a heavy atom into the quencher.[32] Therefore, an external heavy atom effect could be expected as the number of chlorine atoms on the benzylamine forming the exciplex increases. Since the exciplex decay times do not change with the number of chlorine atoms, heavy atom effects can be discarded.

There are not many alternatives to explain the exciplexes' fluorescence quantum yield dependence on the number of chlorine atoms in the benzylamine. One possibility is that the exciplexes were formed through a precursor that can either evolve to the exciplex or deactivate to the ground state. If in this precursor the chloroaromatic residue were near the exciplex, external heavy atom effects could be present. Ultra fast transient technique studies will be required to understand this problem.

From Table 1 it can be observed that the emission maxima of the intermolecular N–TEA and N–**II** exciplexes are at longer wavelengths than the emission maxima of the intramolecular exciplexes **I** and **VI**, respectively. The theoretical model for complexes of naphthalene with aromatic donors[33,34] has been extended to complexes with aliphatic donors.[35,36] If the amine donor and the naphthalene acceptor are linked by an alkyl chain, the number of spatial positions that the nitrogen can adopt relative to the naphthalene is restricted. Each position is characterized by the distance between the positive charge located on the amino group and the centre of the negative charge located on the naphthalene. The stabilization of the charge transfer state by coulombic interaction, which is the principal contributing state to the exciplex wavefunction, will be different for the loose intermolecular exciplexes and the restricted intramolecular exciplexes. The repulsion energy may also differ. This leads to different exciplex emission maxima. It was experimentally observed by Swinnen *et al.*[26] that the emission maximum of the 1-methylpyrene–TEA exciplex in ethyl ether is located at 500 nm while for 2-(*N*,*N*-dimethylamino)-1-pyren-1-ylethane, which forms an intramolecular exciplex, the maximum is situated at 470 nm. This is an indication that the absence of a chain permits the nitrogen to attain a position that further enhances the coulombic interaction. Therefore, the same conclusions can be extended to the systems under study.

It can be observed from Table 1 that the fluorescence maximum of the intramolecular exciplex formed by **VI** is located at a shorter wavelength than the maximum of **I**. This could be attributed to the benzyl group in **VI** restricting the approach of the amine group to the naphthalene ring even more. Working with space filling molecular models confirms this supposition. In the special case of intramolecular exciplexes like **I** the best geometry of the exciplex is attained with eclipsed methylene groups and a dihedral angle of about −25°.[37] Free rotation of the C–N bonds in compound **VI** moves the benzyl group towards the naphthalene. To avoid at least partially this steric factor the nitrogen centre could move slightly apart from the ring, in this way increasing the distance between the charge centres. Because the benzyl group is near the naphthalene ring, the trichlorobenzyl group in compound **VII** will probably have a favourable conformation for intramolecular terplex formation. This leads to the lack of fluorescence in **VII** and may explain its dechlorination.

From Table 2 it can be observed that all the k_q measured are of the same order of magnitude. The reason for this is that k_q represents an electron transfer reaction between one naphthalene–amine exciplex that is always nearly the same and a trichlorobenzene or a trichlorobenzene residue. The efficiency of formation of HCl is small for all the systems studied and no important differences are observed concerning the intermolecular system.

Conclusions

The use of bifunctional quenchers of naphthalene, such as compound **V**, favours terplex formation by providing a high local concentration of the second quencher molecule close to the initially formed exciplex. However, a second bifunctional molecule **V** is necessary to produce HCl. This is an indication that in the exciplex initially formed the trichlorobenzene moiety is not near the naphthalene molecule because of the short linkage between **D** and TCB in **V**. To form the terplex TCB–**N**–**D**, that is the precursor to HCl formation, a second molecule of **V** is necessary. With compound **VII** it is possible to form the terplex TCB–**N**–**D** intramolecularly resulting in HCl production and the lack of fluorescence in this compound.

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