

# Internal conversion with 4-(azetidinyl)benzotrioles in alkane solvents. Influence of fluoro substitution

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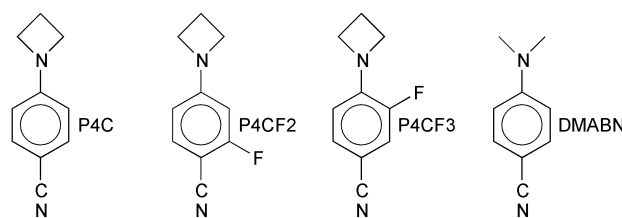
The introduction of a fluoro-substituent in the phenyl ring of 4-(1-azetidinyl)benzotriole (P4C) leads to smaller fluorescence quantum yields  $\Phi_f$  and shorter decay times  $\tau$  in alkane solvents (cyclopentane, n-hexadecane, n-hexane and 2-methylpentane). In cyclopentane at 25 °C,  $\Phi_f$  and  $\tau$  equal 0.02 and 0.14 ns for 2-fluoro-4-(1-azetidinyl)benzotriole (P4CF2) and 0.11 and 0.85 ns for 3-fluoro-4-(1-azetidinyl)benzotriole (P4CF3), as compared with 0.27 and 4.55 ns for P4C. The fluorescence originates from a locally excited (LE) state and dual fluorescence due to intramolecular charge transfer is not observed for the three aminobenzotrioles at any temperature in the alkane solvents. By measuring the yields of intersystem crossing  $\Phi_{ISC}$ , it follows that this enhancement of the radiationless deactivation of the first excited singlet state  $S_1$  is due to thermally activated internal conversion (IC). The IC yield  $\Phi_{IC}$  in cyclopentane at 25 °C, as an example, is considerably larger for P4CF2 (0.93) than for P4CF3 (0.35) and of minor importance for P4C (0.03). The IC activation energies  $E_{IC}$  of P4CF2 (12.6 kJ mol<sup>-1</sup>), P4CF3 (19.3 kJ mol<sup>-1</sup>) and P4C (38.1 kJ mol<sup>-1</sup>) in cyclopentane were determined by fitting  $\tau$  measured as a function of temperature, together with data for  $\Phi_f$  and  $\Phi_{ISC}$ . Similar  $E_{IC}$  values were obtained in n-hexane and n-hexadecane. These data show that the increase in IC efficiency from P4C via P4CF3 to P4CF2 is caused by a decrease in  $E_{IC}$ . The radiative rate constants  $k_f$  in cyclopentane of P4CF2 and P4CF3 are about twice that of P4C, probably due to the mixing of the  $S_2(^1L_a, CT)$  and  $S_1(^1L_b)$  states of P4C caused by the molecular asymmetry introduced by the F-substituents. It is assumed that the lowering of the IC barriers in P4CF2 and P4CF3 is governed by an F-substituent-dependent difference in the energies of the molecular configuration of the azetidinylbenzotrioles that can be reached in  $S_1$  as compared with those in  $S_0$ .

## Introduction

In nonpolar alkane solvents, the fluorescence spectra of 4-(dimethylamino)benzotriole (DMABN)<sup>1–4</sup> and related molecules such as P4C<sup>5</sup> consist of a single fluorescence band originating from a LE state. There is experimental evidence that appreciable dual fluorescence and ICT does not take place under these conditions.<sup>1–6</sup> In accordance with this observation, the fluorescence decays of both 4-aminobenzotrioles in alkane solvents are single exponential.<sup>3,7</sup>

With DMABN in n-hexane at 25 °C, the sum of the fluorescence quantum yield  $\Phi_f$  and the yield of intersystem crossing  $\Phi_{ISC}$  is close to unity,<sup>8</sup> showing that internal conversion is not an important deactivation pathway of its  $S_1$  state in this solvent at room temperature. Efficient thermally activated internal conversion has, however, been observed with a number of other aromatic amines: 3,5-dimethyl-4-(methylamino)benzotriole (MHD),<sup>9</sup> 1-(dialkylamino)naphthalenes,<sup>10–15</sup> a series of 4-substituted 1-(dimethylamino)naphthalenes<sup>15</sup> and 9-(dimethylamino)anthracenes.<sup>16</sup> It has been shown that the occurrence of this internal conversion is governed by the twist angle of the amino group relative to the plane of the aromatic moiety, as well as by the energy gap  $\Delta E(S_1, S_2)$  between the two lowest

excited singlet states.<sup>12–16</sup> The IC reaction has been assumed to proceed from  $S_1$  to  $S_0$  via a conical intersection.<sup>14,15,17</sup>



During an investigation of the influence of fluoro substitution in the phenyl ring of aminobenzotrioles on the efficiency of ICT in the singlet excited state,<sup>18</sup> it was found that with P4CF2 and P4CF3 in alkane solvents the F-substitution opens up an efficient internal conversion channel. The investigation of the photophysics of the three molecules P4CF<sub>x</sub> (P4CF2, P4CF3 and P4C) in cyclopentane, n-hexane and n-hexadecane as a function of temperature is reported here.

## Experimental

P4CF2 (mp 81–84 °C) and P4CF3 (mp 81–84 °C) were synthesized in a reaction between azetidine (Aldrich) and 2,4-difluorobenzotriole (Lancaster) or 3,4-difluorobenzotriole (Lancaster), respectively. The structures of P4CF2 and P4CF3 were verified by analysis of their <sup>13</sup>C and <sup>1</sup>H NMR spectra, as well as by X-ray diffraction.<sup>19</sup> The synthesis procedure used for

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P4C has been described previously<sup>4,20</sup> and DMABN was obtained from Aldrich. For the four aminobenzonitriles, high performance liquid chromatography (HPLC) was the last purification step.

The alkane solvents cyclopentane, n-hexadecane and 2-methylpentane were chromatographed over Al<sub>2</sub>O<sub>3</sub> just prior to use, whereas n-hexane (Merck, Uvasol) was used as received. The solutions, with an absorbance between 0.4 and 0.6 for the maximum of the first band in the absorption spectrum, were deaerated by bubbling with nitrogen for 15 min.

The fluorescence spectra were measured with a quantum-corrected Shimadzu RF-5000PC spectrofluorometer. Fluorescence quantum yields  $\Phi_f$ , with an estimated reproducibility of 2%, were determined relative to quinine sulfate in 1.0 N H<sub>2</sub>SO<sub>4</sub> ( $\Phi_f=0.546$  at 25 °C),<sup>21</sup> with equal absorbances at the excitation wavelength. The difference in refractive index between the standard solution and the alkanes was neglected.<sup>22,23</sup> In the determination of the temperature dependence of  $\Phi_f$ , the change in absorbance with temperature was measured and its nonlinear influence on the fluorescence intensity was taken into account. The fluorescence decay times were determined with picosecond laser (excitation wavelength  $\lambda_{exc}$ : 276 or 297 nm) or nanosecond ( $\lambda_{exc}$ : 296 nm) flashlamp single-photon counting (SPC) set-ups. These set-ups and the analysis procedure of the fluorescence decays have been described previously.<sup>20,24</sup> The instrument response function of the laser systems have a half-width of 18–25 ps.

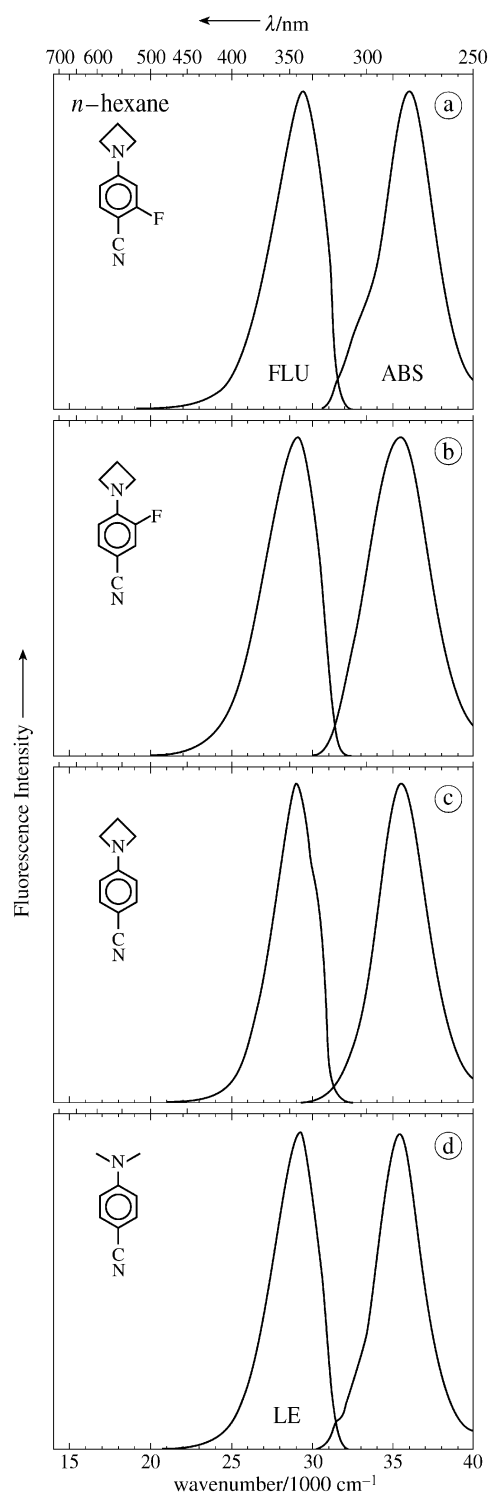
The yields  $\Phi_{ISC}$  of the intersystem crossing from the equilibrated S<sub>1</sub> state to the lowest triplet state T<sub>1</sub> were measured by T–T absorption, using a method based on triplet–triplet energy transfer with perylene as the acceptor.<sup>25,26</sup> N-Methyl-1,8-naphthalimide was used as a reference substance, with  $\Phi_{ISC}=0.96$  in n-hexane at 25 °C, measured against fluorenone ( $\Phi_{ISC}=1.00$ )<sup>27</sup> with 308 and 337 nm excitation. The solutions used in these experiments were degassed employing the freeze–pump–thaw method (5 cycles). The molar absorption coefficients of the triplet state of P4CF<sub>2</sub>, P4CF<sub>3</sub> and P4C in n-hexane, see Fig. 2 and Table 1 below, were determined relative to that of benzophenone triplet (6600 M<sup>-1</sup> cm<sup>-1</sup> at 525 nm)<sup>28</sup> measured at the same absorbance (around 0.7) in acetonitrile at 22 °C.

The parameters for the photophysical processes of the molecules P4CF<sub>x</sub> were obtained by a global nonlinear least-squares method, with the sum of the weighted squares of the residuals  $S = \sum_j \sum_i w_{ij} (\ln y_{ij} - \ln y_{ij}^{exp})^2$  as the target function. In the expression for  $S$ ,  $w$  is a weighting factor and  $y$  is a response function (fluorescence lifetime, fluorescence quantum yield and triplet yield). The index  $j$  refers to the response functions, the index  $i$  counts the experimental points for each response function and the index exp indicates that the quantity is an experimental value. The factor  $w$  is proportional to the inverse of the estimated dispersion of the experimental data. By using logarithms,  $S$  no longer depends on the scaling of the response function.

## Results and discussion

### Fluorescence and absorption spectra of P4CF<sub>2</sub>, P4CF<sub>3</sub>, P4C and DMABN

The fluorescence spectra of P4CF<sub>2</sub>, P4CF<sub>3</sub>, P4C and DMABN in n-hexane at 25 °C consist of a single LE emission band, see Fig. 1, without any indication of the presence of an additional red-shifted charge transfer band. Similar observations are made in cyclopentane, 2-methylpentane and n-hexadecane. This absence of dual fluorescence for P4CF<sub>x</sub> in the alkane solvents holds over a large temperature range, between –90 °C (cyclopentane) and 284 °C (n-hexadecane).



**Fig. 1** Fluorescence and absorption spectra (normalised) in n-hexane at 25 °C of (a) P4CF<sub>2</sub>, (b) P4CF<sub>3</sub>, (c) P4C and (d) DMABN. The fluorescence consists of an emission from a LE state.

Fluoro-substitution in the phenyl ring leads to changes in the absorption spectra of P4CF<sub>2</sub> and P4CF<sub>3</sub> as compared with that of P4C, see Fig. 1. In the spectrum of P4CF<sub>2</sub>, the S<sub>1</sub> band is clearly visible as a shoulder at the low-energy side of the main S<sub>2</sub> transition,<sup>3,29</sup> whereas with P4CF<sub>3</sub> the S<sub>1</sub> band is largely covered by the S<sub>2</sub> absorption. This indicates that the energy difference  $\Delta E(S_1, S_2)$  between the two lowest excited singlet states is influenced by F-substitution. Whereas with P4CF<sub>2</sub> a larger value for  $\Delta E(S_1, S_2)$  is observed than for P4C, the opposite is the case for P4CF<sub>3</sub>.<sup>3,29</sup>

**Table 1** Fluorescence quantum yields  $\Phi_f$ , yields of intersystem crossing  $\Phi_{ISC}$  and internal conversion  $\Phi_{IC}$ , molar absorption coefficients  $\epsilon^{\max}$  and  $\epsilon^{\max}(\text{TT})$ , maxima  $\nu^{\max}$  of the absorption and fluorescence spectra and energy  $E(S_1)$  for P4CF2, P4CF3, P4C and DMABN in alkane solvents at 25 °C

	Solvent	P4CF2	P4CF3	P4C	DMABN
$\Phi_f$	n-Hexane	0.017	0.114	0.255	0.18 <sup>a</sup>
	Cyclopentane	0.016	0.112	0.275	
	n-Hexadecane	0.023	0.134	0.285	
$\Phi_{ISC}$	n-Hexane	0.09	0.58	0.67	0.76 <sup>a</sup>
$\Phi_{IC}(=1-\Phi_f-\Phi_{ISC})$	n-Hexane	0.89	0.31	0.08	0.06
$\epsilon^{\max}/\text{M}^{-1}\text{cm}^{-1}$	n-Hexane	30 405	24 610	29 950	28 860
$\epsilon^{\max}(\text{TT})/\text{M}^{-1}\text{cm}^{-1}$	Cyclopentane	7700	7650	9400	
$\nu^{\max}(\text{TT-abs})/1000\text{cm}^{-1}$		27.2	28.2	27.3	
$\nu^{\max}(\text{abs})/1000\text{cm}^{-1}$	n-Hexane	36.11	35.38	35.54	35.53
$\nu^{\max}(\text{flu})/1000\text{cm}^{-1}$	n-Hexane	29.47	29.09	29.09	29.33
$E(S_1)/1000\text{cm}^{-1}$	n-Hexane	31.63	31.37	31.47	31.65

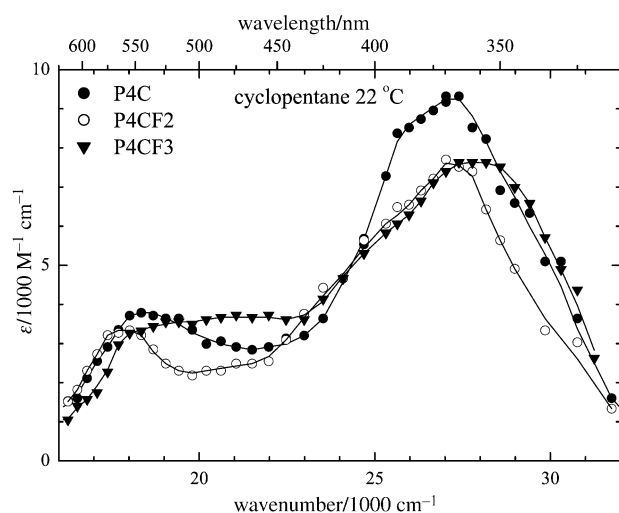
<sup>a</sup> From ref. 8. <sup>b</sup> Molar absorption coefficient at the maximum  $\nu^{\max}(\text{TT-abs})$  of the triplet-triplet absorption spectrum, see Fig. 2. <sup>c</sup> The energy of the crossing of the absorption and fluorescence spectra, see Fig. 1.

The smaller value of the molar absorption coefficient  $\epsilon_{\max}$  at the absorption maximum for P4CF3 as compared with P4CF2 and P4C in n-hexane (Table 1), could indicate that the presence of the *ortho*-F-substituent in P4CF3 leads to a twist of the azetidiny group with respect to the plane of the phenyl ring.<sup>9</sup> X-ray measurements<sup>19</sup> and DFT calculations<sup>30</sup> are in progress to determine the molecular structures of the P4CF<sub>x</sub> molecules.

#### Yields of fluorescence, intersystem crossing and internal conversion at 25 °C

F-substitution into the phenyl ring of P4C leads to a considerable lowering of the fluorescence quantum yield  $\Phi_f$  in n-hexane at 25 °C, from 0.26 (P4C) to 0.11 (P4CF3) and 0.02 (P4CF2), see Table 1. A similar result is obtained in cyclopentane and n-hexadecane (Table 1) as well as in 2-methylpentane.

In order to establish the nature of the nonradiative decay processes in the three 4-(azetidiny)benzonitriles, the intersystem crossing yields  $\Phi_{ISC}$  were determined in n-hexane at 25 °C (Table 1): 0.09 (P4CF2), 0.58 (P4CF3) and 0.67 (P4C). The T-T absorption spectra of P4CF2 and P4CF3 in cyclopentane are depicted in Fig. 2. As there is no evidence that the fluorescence quantum yields at this temperature are reduced by photochemical reactions, these results show that substantial internal conversion takes place with the two F-substituted aminobenzonitriles, with yields  $\Phi_{IC}(=1-\Phi_f-\Phi_{ISC})$  of 0.89



**Fig. 2** Triplet-triplet absorption spectra of P4C, P4CF2 and P4CF3 in cyclopentane at 22 °C.

(P4CF2), 0.31 (P4CF3) and 0.08 (P4C). It follows from these data that IC is the major deactivation pathway for P4CF2, whereas ISC is the main decay channel for P4CF3, P4C and DMABN in the alkanes at 25 °C.

#### Fluorescence decay times at 25 °C

The fluorescence decays of P4C, P4CF2 and P4CF3 in n-hexane at 25 °C are shown in Fig. 3. The decays are single exponential, supporting the conclusion reached from the fluorescence spectra (Fig. 1) that dual fluorescence does not occur with these molecules in the alkane solvents investigated here. The decay time  $\tau$  of P4CF2 is much shorter (0.137 ns) than that of P4C (4.57 ns), whereas with P4CF3 an intermediate value of 0.883 ns is found (Table 2). From these decay times and the yields of fluorescence, intersystem crossing and internal conversion (Table 1), the rate constants of these deactivation processes can be determined by using the relationship  $k_i = \Phi_i/\tau$ , see Table 2.

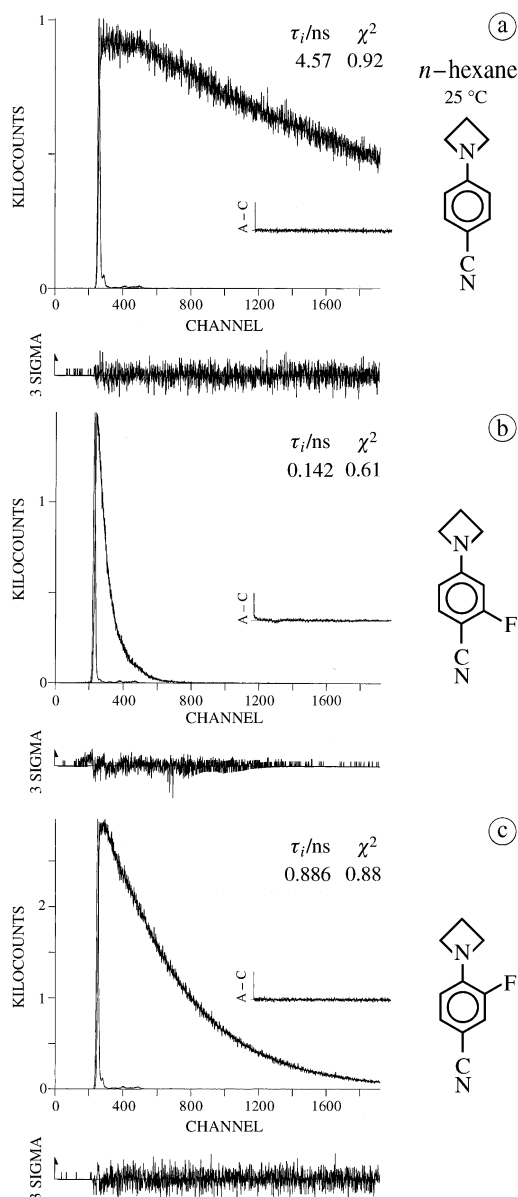
#### Rate constants for internal conversion, intersystem crossing and fluorescence at 25 °C

The rate constant for internal conversion  $k_{IC}$  in n-hexane at 25 °C has a considerably larger value for P4CF2 ( $6.3 \times 10^9\text{ s}^{-1}$ ) than for P4CF3 ( $0.4 \times 10^9\text{ s}^{-1}$ ), whereas for P4C a much smaller value is obtained ( $0.02 \times 10^9\text{ s}^{-1}$ ). The fluorescence decay times  $\tau$  of P4CF2 and P4CF3 are also shortened with respect to that of P4C by a larger ISC rate constant  $k_{ISC}$  of  $0.64 \times 10^9\text{ s}^{-1}$  as compared with  $0.16 \times 10^9\text{ s}^{-1}$ . In addition, the radiative rate constants  $k_f$  in n-hexane at 25 °C of P4CF2 ( $11.9 \times 10^7\text{ s}^{-1}$ ) and P4CF3 ( $12.9 \times 10^7\text{ s}^{-1}$ ) are larger than that of P4C ( $5.6 \times 10^7\text{ s}^{-1}$ ), probably due to the coupling of the  $S_2(^1L_a, \text{CT})$  and  $S_1(^1L_b)$  states of P4C,<sup>5,29</sup> caused by the molecular asymmetry introduced by the F-substituents.

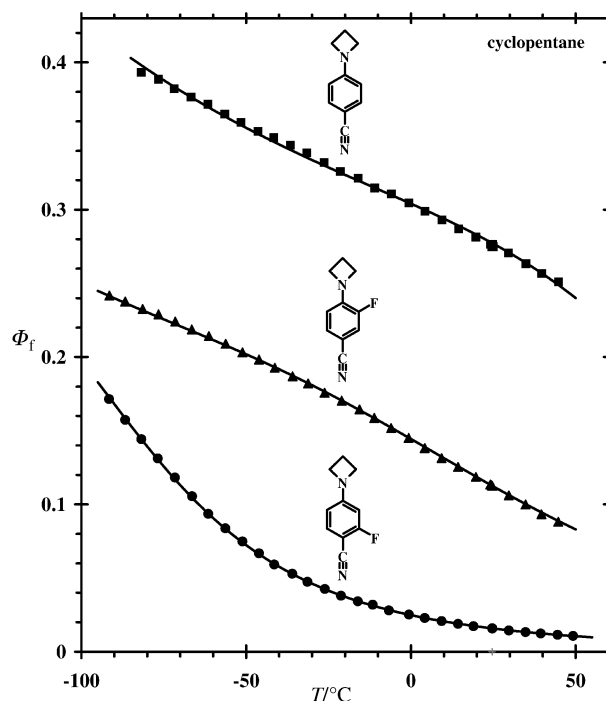
#### $\Phi_f$ and $\Phi_{ISC}$ as a function of temperature

The fluorescence quantum yields  $\Phi_f$  of the three azetidinybenzonitriles P4CF<sub>x</sub>, measured as a function of temperature in cyclopentane, are presented in Fig. 4. It is seen that  $\Phi_f$  is considerably smaller for P4CF2 than for P4C over the entire temperature range, decreasing from 0.17 at -92 °C to 0.01 at 45 °C (P4CF2), as compared with a decrease from 0.39 to 0.26 for P4C. P4CF3 takes up an intermediate position, with a decrease in  $\Phi_f$  from 0.24 to 0.09 between these two temperatures.

The temperature dependence of the intersystem crossing yield  $\Phi_{ISC}$  relative to that at 25 °C was determined for P4CF2



**Fig. 3** Single exponential fluorescence decays of (a) P4C, (b) P4CF2 and (c) P4CF3 in n-hexane at 25 °C. The weighted deviations, the autocorrelation functions A–C and the values for  $\chi^2$  are also indicated. Excitation wavelength: 297 nm.



**Fig. 4** Fluorescence quantum yields  $\Phi_f$  as a function of temperature for P4C, P4CF2 and P4CF3 in cyclopentane. The lines through the data points represent the fitting resulting from the procedure described in the text (eqn. (1) and (2)).

and P4CF3 in cyclopentane, see Fig. 5. For P4CF2, this ratio  $\Phi_{ISC}/\Phi_{ISC}(25)$  decreases strongly from 7.3 at  $-81$  °C to 0.7 at  $49$  °C, whereas this ratio decreases from 1.0 to 0.8 between  $23$  and  $52$  °C in the case of P4CF3.

The  $\Phi_f$  and  $\Phi_{ISC}/\Phi_{ISC}(25)$  data will be used in the fitting procedure for the fluorescence decay times  $\tau$  of the P4CF $x$  compounds measured as a function of temperature, which will be treated in the following sections.

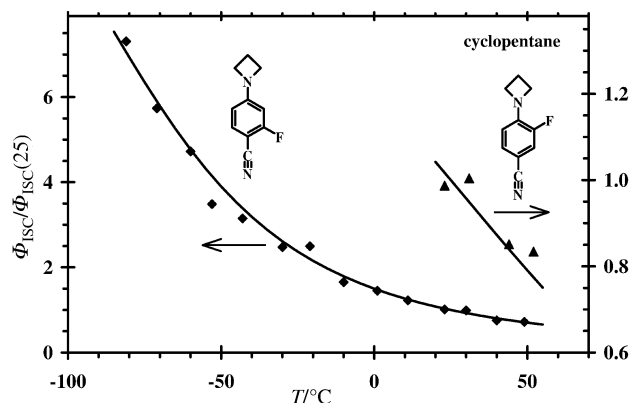
#### IC and ISC Arrhenius parameters from temperature dependence of fluorescence decay times. Fitting methodology

With 1-(dimethylamino)naphthalene (DMAN) in isopentane<sup>31</sup> and n-hexane,<sup>14,31</sup> the IC and ISC activation energies  $E_{IC}$  and  $E_{ISC}$  and also the preexponential factors  $k_{IC}^0$  and  $k_{ISC}^0$  have been determined from the fluorescence decay times  $\tau$  measured as a function of temperature. This has been done by fitting the  $\tau$  data with an equation in which the rate constants  $k_{IC}$  and  $k_{ISC}$  are given in Arrhenius form and the radiative rate

**Table 2** Fluorescence decay times  $\tau$  and rate constants for fluorescence ( $k_f$ ), intersystem crossing ( $k_{ISC}$ ) and internal conversion ( $k_{IC}$ ) of P4CF2, P4CF3, P4C and DMABN in alkane solvents at 25 °C

	Solvent	P4CF2	P4CF3	P4C	DMABN
$\tau/\text{ns}$	Cyclopentane	0.137	0.846	4.55	3.40
	n-Hexane	0.141	0.883	4.57	3.45
	n-Hexadecane	0.195	0.984	4.53	3.36
	2-Methylpentane	0.130	0.847	4.58	
$k_f/10^7 \text{ s}^{-1}$ <sup>a</sup>	Cyclopentane	11.7	13.2	6.0	
	n-Hexane	12.1	12.9	5.6	5.3
	n-Hexadecane	11.8	13.6	6.3	
$k_{IC}/10^9 \text{ s}^{-1}$ <sup>c</sup>	n-Hexane	6.3 (6.5)	0.35 (0.39)	0.02 (0.01)	0.02
$k_{ISC}/10^9 \text{ s}^{-1}$ <sup>b</sup>	n-Hexane	0.64 (0.37)	0.66 (0.61)	0.15 (0.15)	0.22

<sup>a</sup>  $k = \Phi_f/\tau$ . <sup>b</sup>  $k_{ISC} = \Phi_{ISC}/\tau$ . <sup>c</sup>  $k_{IC} = \Phi_{IC}/\tau$ . The values in parentheses for  $k_{ISC}$  and  $k_{IC}$  are determined by a fitting procedure involving the fluorescence decay times  $\tau$  measured as a function of temperature, see text (eqn. (1)) and Tables 3 and 4.



**Fig. 5** The temperature dependence of the intersystem crossing yield  $\Phi_{\text{ISC}}$  relative to that at 25°C,  $\Phi_{\text{ISC}}(25)$ , for P4CF2 and P4CF3 in cyclopentane.

constant  $k_f$  is taken to be independent of temperature.<sup>14,15</sup> With the present molecules P4CF $x$  a similar fitting procedure will be followed.

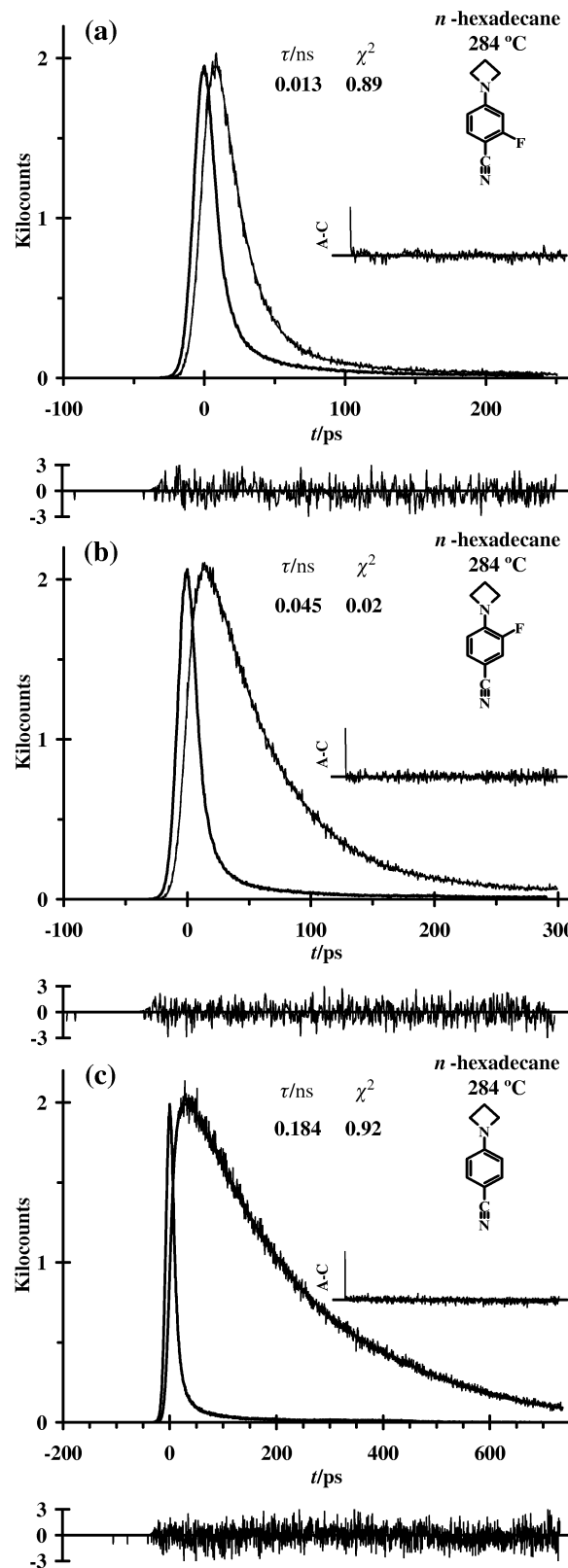
For 1DMAN in isopentane, with  $E_{\text{IC}} = 18.1 \text{ kJ mol}^{-1}$  and  $E_{\text{ISC}} = 5.0 \text{ kJ mol}^{-1}$ ,<sup>31</sup> IC starts to completely dominate the fluorescence decay at temperatures above  $-30^\circ\text{C}$  ( $\Phi_{\text{IC}} = 0.86$ ,  $\Phi_{\text{ISC}} = 0.10$ ). ISC, on the other hand, becomes the main deactivation process at temperatures below  $-110^\circ\text{C}$  ( $\Phi_{\text{ISC}} = 0.64$ ,  $\Phi_{\text{IC}} = 0.08$ ). It is clear that under these conditions,  $E_{\text{IC}}$  and  $E_{\text{ISC}}$  can both be determined by fitting the decay times over the temperature range from 25 down to  $-160^\circ\text{C}$ . In the case of 1-(*N*-azetidyl)naphthalene, the larger value of  $E_{\text{IC}}$  ( $26 \text{ kJ mol}^{-1}$ ) already stops the IC process in *n*-hexane at around  $-40^\circ\text{C}$ , as seen from the temperature dependence of the fluorescence quantum yields.<sup>14</sup> With 1DMAN in *n*-hexane (mp  $-95^\circ\text{C}$ ), however, the ISC low-temperature limit cannot be reached. Therefore, the value obtained for  $E_{\text{ISC}}$  in isopentane ( $5.0 \text{ kJ mol}^{-1}$ ) was kept constant during the fitting of the  $\tau$  data.<sup>14</sup> The possibility to determine both  $E_{\text{IC}}$  and  $E_{\text{ISC}}$  by this method obviously depends on the difference in magnitude between these activation energies and the accessible temperature range.

#### Temperature dependence of fluorescence decay times of P4CF $x$

The fluorescence decays of P4CF2, P4CF3 and P4C were measured as a function of temperature in cyclopentane, *n*-hexane and *n*-hexadecane. The decays are single exponential at all temperatures measured, as shown in Fig. 6 for the solvent *n*-hexadecane at  $284^\circ\text{C}$  (see also Fig. 3). With the P4CF $x$  molecules in 2-methylpentane, in contrast to cyclopentane and *n*-hexane, the fluorescence decays become double exponential upon cooling below  $-10^\circ\text{C}$ , presumably due to solubility problems, such as the formation of aggregates and microcrystals. From the decay times, combined in some cases with  $\Phi_f$  and  $\Phi_{\text{ISC}}$  data, as mentioned above, the IC and ISC Arrhenius parameters can both be determined by fitting the experimental data for  $\tau$  and  $\Phi_i$  (eqn. (1) and (2)). This is possible when IC and ISC dominate the deactivation process of  $S_1$  in different temperature ranges as a consequence of sufficiently different activation energies  $E_{\text{IC}}$  and  $E_{\text{ISC}}$ . In less favourable cases,  $E_{\text{ISC}}$  must be fixed, as described in the previous section.

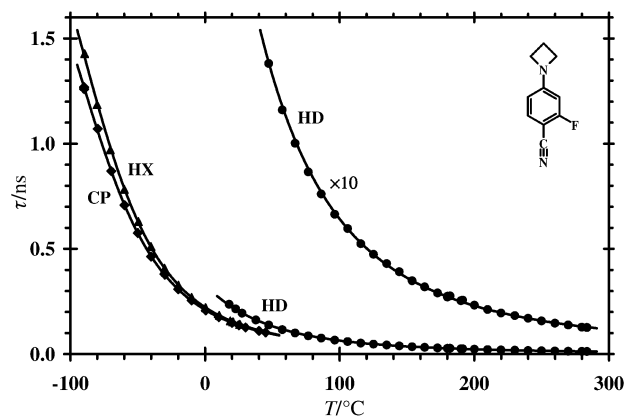
$$1/\tau = k_f + k_{\text{IC}} + k_{\text{ISC}} = k_f(0)n^x + k_{\text{IC}}^0 \exp(-E_{\text{IC}}/RT) + k_{\text{ISC}}^0 \exp(-E_{\text{ISC}}/RT) \quad (1)$$

$$\Phi_i = k_i \tau \quad (i = f, \text{IC}, \text{ISC}) \quad (2)$$



**Fig. 6** Single exponential fluorescence decay curves with decay time  $\tau$  of (a) P4CF2, (b) P4CF3 and (c) P4C in *n*-hexadecane at  $284^\circ\text{C}$ . The time scale equals 0.5 ps per channel. The weighted deviations, the autocorrelation functions A-C, and the values for  $\chi^2$  are also indicated. Excitation wavelength: 276 nm.

In eqn. (1), the temperature dependence of the radiative rate constant  $k_f$  is calculated from that of the refractive index  $n$  by using the expression  $k_f = k_f(0)n^x$  ( $x = 2$  or  $3$ ),<sup>32,33</sup> in which  $k_f(0)$  does not depend on temperature.



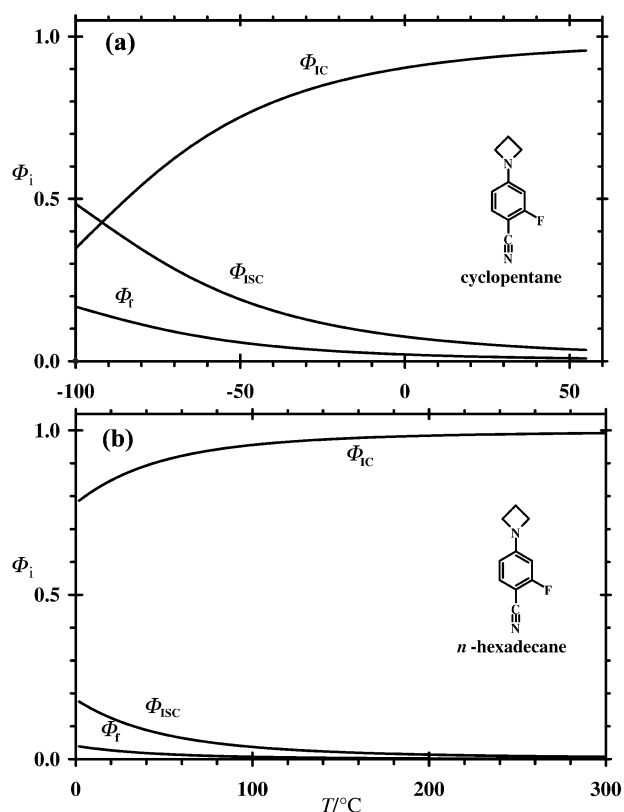
**Fig. 7** Plots of the fluorescence decay times  $\tau$  of P4CF2 in cyclopentane (CP), n-hexane (HX) and n-hexadecane (HD) as a function of temperature. The lines through the data points represent the fitting resulting from the procedure described in the text (eqn. (1) and (2)).

### P4CF2. Fluorescence decay times in cyclopentane, n-hexane and n-hexadecane as a function of temperature

In the previous sections it was shown that with P4CF2 in cyclopentane, n-hexane and n-hexadecane at 25 °C, IC is the most important decay channel for the  $S_1$  state, next to ISC and LE fluorescence. In order to investigate the rate parameters of these deactivation processes, the fluorescence decays of P4CF2 in the three alkane solvents were measured as a function of temperature, see Fig. 7.

**P4CF2 in cyclopentane and n-hexane.** The fluorescence decay time  $\tau$  of P4CF2 in cyclopentane decreases from 1.3 ns at  $-90$  °C to 120 ps at 45 °C (Fig. 7). This data set was fitted by using eqn. (1) (with  $k_f \sim n^3$ ), also taking into account the fluorescence quantum yields measured as a function of temperature (Fig. 4) as well as the relative ISC yields  $\Phi_{ISC}/\Phi_{ISC}(25)$  determined between  $-81$  and 49 °C (Fig. 5). The good quality of the fitting is shown by the line through the data points for  $\tau$  (Fig. 7),  $\Phi_f$  (Fig. 4) and  $\Phi_{ISC}/\Phi_{ISC}(25)$  (Fig. 5).

From this fit the following Arrhenius parameters and  $k_f(0)$  value result:  $E_{IC} = 12.6$  kJ mol $^{-1}$ ,  $k_{IC}^0 = 1.1 \times 10^{12}$  s $^{-1}$ ,  $E_{ISC} = 0.5$  kJ mol $^{-1}$ ,  $k_{ISC}^0 = 0.5 \times 10^9$  s $^{-1}$  and  $k_f(0) = 4.1 \times 10^7$  s $^{-1}$ , see Table 3. For the decay times  $\tau$  of P4CF2 in n-hexane measured between  $-90$  and 65 °C, together with  $\Phi_f$  at 25 °C (Table 1), the fitting procedure using eqn. (1) (with  $k_f \sim n^3$ ) gives similar



**Fig. 8** Temperature dependence of the internal conversion yield  $\Phi_{IC}$ , the intersystem crossing yield  $\Phi_{ISC}$  and the fluorescence quantum yield  $\Phi_f$  of P4CF2 in (a) cyclopentane and (b) n-hexadecane. See text.

results for the Arrhenius parameters and  $k_f(0)$ , see Table 3. In this case, the value for  $E_{ISC}$  (0.5 kJ mol $^{-1}$ ) obtained in cyclopentane was kept constant during the fitting.

**$\Phi_{IC}$ ,  $\Phi_{ISC}$  and  $\Phi_f$  for P4CF2 in cyclopentane.** Using the Arrhenius parameters and  $k_f(0)$  obtained in the previous section, the temperature dependence of the yields  $\Phi_{IC}$ ,  $\Phi_{ISC}$  and  $\Phi_f$  for P4CF2 in cyclopentane can be calculated, see Fig. 8(a) and Table 4. These data show that  $\Phi_{IC}$  increases from 0.35 at  $-90$  °C to 0.95 at 45 °C, whereas  $\Phi_{ISC}$  decreases strongly from 0.47 to 0.04 between these two temperatures. Also  $\Phi_f$  decreases from 0.18 to 0.01 over this temperature interval (Fig. 8(a)). It clearly follows from these

**Table 3** Activation energies  $E_i$  and preexponential factors  $k_i^0$  of the internal conversion (IC) and intersystem crossing (ISC) radiationless decay channels and the temperature-independent factor  $k_f(0)$  of the radiative rate constant  $k_f = k_f(0)n^3$  (eqn. (1), see text) for P4CFx in three alkane solvents. For P4CF2 and P4CF3 in cyclopentane and for P4C in n-hexadecane the results obtained by using  $k_f = k_f(0)n^2$  in eqn. (1) are also listed. The values for  $E_{IC}$  and  $E_{ISC}$  in parentheses are kept fixed in the fitting procedure described in the text (eqn. (1))

	Solvent	$E_{IC}/\text{kJ mol}^{-1}$	$k_{IC}^0/10^{12} \text{ s}^{-1}$	$E_{ISC}/\text{kJ mol}^{-1}$	$k_{ISC}^0/10^9 \text{ s}^{-1}$	$k_f(0)/10^7 \text{ s}^{-1}$
P4CF2	Cyclopentane	12.6	1.1	0.5	0.5	4.1
	$k_f = k_f(0)n^2$	12.7	1.1	0.5	0.5	5.9
	n-Hexane	13.1	1.3	(0.5)	0.5	4.6
	n-Hexadecane	15.5	2.2	(0.5)	0.7	3.9
P4CF3	Cyclopentane	19.3	1.0	1.0	1.0	4.8
	$k_f = k_f(0)n^2$	19.1	1.0	1.1	1.0	6.9
	n-Hexane	19.2	0.9	(1.0)	0.9	5.0
	n-Hexadecane	24.0	3.7	(1.0)	1.0	4.6
P4C	n-Hexadecane	38.1	19	(1.5)	0.3	2.2
		38.5	21	2.1	0.4	2.1
	$k_f = k_f(0)n^2$	38.1	19	(1.3)	0.3	3.1
	Cyclopentane	(38.1)	34	1.5	0.3	2.2
		(38.5)	41	1.5	0.3	2.2
	n-Hexane	(38.1)	49	1.5	0.3	2.2
		(38.5)	59	1.5	0.28	2.2

**Table 4** Fluorescence quantum yields  $\Phi_f$ , yields of internal conversion  $\Phi_{IC}$  and intersystem crossing  $\Phi_{ISC}$  and radiative rate constant  $k_f$  for P4CF2, P4CF3, P4C in cyclopentane, n-hexane and n-hexadecane at 25 °C, calculated by using the parameters  $E_{ISC}$ ,  $k_{ISC}^0$ ,  $k_{IC}^0$  and  $k_f(0)$  from Table 3 for the  $E_{IC}$  value listed in the last column

	Solvent <sup>a</sup>	$\Phi_f$	$\Phi_{IC}$	$\Phi_{ISC}$	$k_f/10^7 \text{ s}^{-1} \text{ }^b$	$E_{IC}/\text{kJ mol}^{-1} \text{ }^b$
P4CF2	Cyclopentane	0.016	0.925	0.060	11.4	12.6
	n-Hexane	0.017	0.930	0.053	11.9	13.1
	n-Hexadecane	0.023	0.866	0.111	11.5	15.5
P4CF3	Cyclopentane	0.112	0.355	0.533	13.3	19.3
	n-Hexane	0.114	0.347	0.539	12.9	19.2
	n-Hexadecane	0.133	0.234	0.633	13.4	24.0
P4C	Cyclopentane	0.275	0.033	0.692	6.0	38.1
	n-Hexane	0.255	0.048	0.697	5.6	38.1
	n-Hexadecane	0.285	0.018	0.697	6.4	38.1

<sup>a</sup> Solvent refractive index at 25 °C: 1.4034 (cyclopentane), 1.3722 (n-hexane), 1.4323 (n-hexadecane). <sup>b</sup> See Table 3.

results that IC dominates in the high-temperature range and ISC becomes more important at the lower temperatures. This has as its consequence that both  $E_{IC}$  and  $E_{ISC}$  are accessible from the fitting of  $\tau$  by eqn. (1), see above, as IC and ISC determine the fluorescence decay at the high- and low-temperature limits, respectively.

**P4CF2 in n-hexadecane.** The fluorescence decay time of P4CF2 in n-hexadecane decreases strongly upon increasing the temperature, from 240 ps at 20 °C to 13 ps at 284 °C, see Fig. 6 and 7. The line through the set of decay times in Fig. 7 represents the result of fitting these data by using eqn. (1) (with  $k_f \sim n^3$ ). As ISC cannot be accurately determined from the decay times of P4CF2 in n-hexadecane, due to the relatively high melting point (18 °C) of the solvent, see previous sections, the value of  $E_{ISC}$  obtained for cyclopentane (0.5 kJ mol<sup>-1</sup>, Table 3) was taken as a fixed value in this fitting. By this procedure the following data result (Table 3):  $E_{IC} = 15.5 \text{ kJ mol}^{-1}$ ,  $k_{IC}^0 = 2.2 \times 10^{12} \text{ s}^{-1}$ ,  $k_{ISC}^0 = 0.7 \times 10^9 \text{ s}^{-1}$  and  $k_f(0) = 3.9 \times 10^7 \text{ s}^{-1}$ .

Based on these data, the yields  $\Phi_{IC}$ ,  $\Phi_{ISC}$  and  $\Phi_f$  can again be calculated for P4CF2 in n-hexadecane (Fig. 8(b)). It is seen that  $\Phi_{ISC}$  decreases from 0.13 at 18 °C to below 0.01 at 290 °C. From these values for  $\Phi_{ISC}$  it is clear that accurate values for the parameters  $E_{ISC}$  and  $k_{ISC}^0$  cannot be obtained directly from the  $\tau$  data of P4CF2 in n-hexadecane.

**Dependence of  $k_f$  on  $n^3$  or on  $n^2$ .** In the preceding sections the decay times together with the  $\Phi_f$  and  $\Phi_{ISC}$  data of P4CF2 were fitted by using eqn. (1) and the expression  $k_f = k_f(0)n^3$  for the radiative rate constant. Better fits were obtained by adopting the dependence of  $k_f$  on  $n^3$  rather than that on  $n^2$ , although similar values were found for the Arrhenius parameters  $E_{IC}$ ,  $E_{ISC}$ ,  $k_{IC}^0$  and  $k_{ISC}^0$ , as listed in Table 3. The  $n^3$  dependence of  $k_f$  will therefore also be employed for P4CF3 and P4C.

#### P4CF3. Fluorescence decay times in cyclopentane, n-hexane and n-hexadecane as a function of temperature

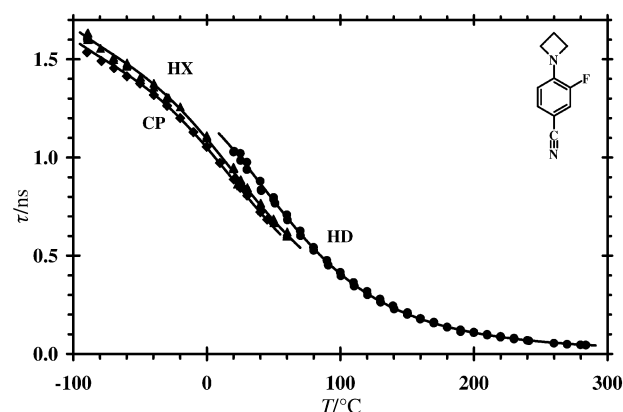
The decay times  $\tau$  of P4CF3 in three solvents (cyclopentane, n-hexane and n-hexadecane) as a function of temperature are plotted in Fig. 9, showing a decrease of  $\tau$  with increasing temperature, but to a smaller extent than that observed with P4CF2 (Fig. 7). In cyclopentane,  $\tau$  decreases from 1.6 ns at -90 °C to 0.66 ns at 45 °C. A similar temperature dependence of  $\tau$  is observed in n-hexane, see Fig. 9. In n-hexadecane, the decay time of P4CF3 gradually decreases from 0.94 ns at 20 °C to 0.045 ns at 284 °C. These decay times were fitted for each of the three solvents by employing eqn. (1) (with  $k_f \sim n^3$ ), following the same procedure as used with P4CF2 in the previous sections. The lines through the three data sets for  $\tau$  in Fig. 9, as well

as for  $\Phi_f$  (Fig. 4) and  $\Phi_{ISC}/\Phi_{ISC}(25)$  (Fig. 5), show that fits of good quality are obtained in the three solvents.

**P4CF3 in cyclopentane and n-hexane.** From the decay times  $\tau$  of P4CF3 measured in cyclopentane between -90 and 45 °C, together with  $\Phi_f$  data over this temperature range (Fig. 4) and the ratios  $\Phi_{ISC}/\Phi_{ISC}(25)$  presented in Fig. 5, the following parameters are obtained:  $E_{IC} = 19.3 \text{ kJ mol}^{-1}$ ,  $k_{IC}^0 = 1.0 \times 10^{12} \text{ s}^{-1}$ ,  $E_{ISC} = 1.0 \text{ kJ mol}^{-1}$ ,  $k_{ISC}^0 = 1.0 \times 10^9 \text{ s}^{-1}$  and  $k_f(0) = 4.8 \times 10^7 \text{ s}^{-1}$ . Similar values result for P4CF3 in n-hexane, keeping the value for  $E_{ISC}$  (1.0 kJ mol<sup>-1</sup>) obtained in cyclopentane constant during the fitting, see Table 3. Fitting the experimental data with eqn. (1) and  $k_f \sim n^2$  does not lead to a significant change in the results, as was found for P4CF2, see Table 3.

Due to the relatively large difference in magnitude between  $E_{IC}$  and  $E_{ISC}$ , ISC predominates in the low-temperature region below -40 °C ( $\Phi_{ISC} = 0.75$  and  $\Phi_{IC} = 0.06$  in cyclopentane), whereas IC becomes more and more important at higher temperatures, with yields  $\Phi_{IC} = 0.47$  and  $\Phi_{ISC} = 0.44$  in cyclopentane at 45 °C. Under these conditions, the IC and the ISC parameters can both be determined by fitting the data for  $\tau$ ,  $\Phi_f$  and  $\Phi_{ISC}/\Phi_{ISC}(25)$ , as discussed previously.

**P4CF3 in n-hexadecane.** For P4CF3 in n-hexadecane, however, fluorescence decay times cannot be measured at sufficiently low temperatures. Therefore, the  $E_{ISC}$  value (1.0 kJ mol<sup>-1</sup>) for cyclopentane was used as a constant value in the fitting of the  $\tau$  and  $\Phi_f(25 \text{ °C})$  data in this solvent. The values so obtained for  $E_{IC}$  (24.0 kJ mol<sup>-1</sup>),  $k_{IC}^0$  ( $3.7 \times 10^{12} \text{ s}^{-1}$ ),  $k_{ISC}^0$  ( $1.0 \times 10^9 \text{ s}^{-1}$ ) and  $k_f(0)$  ( $4.6 \times 10^7 \text{ s}^{-1}$ ), are in



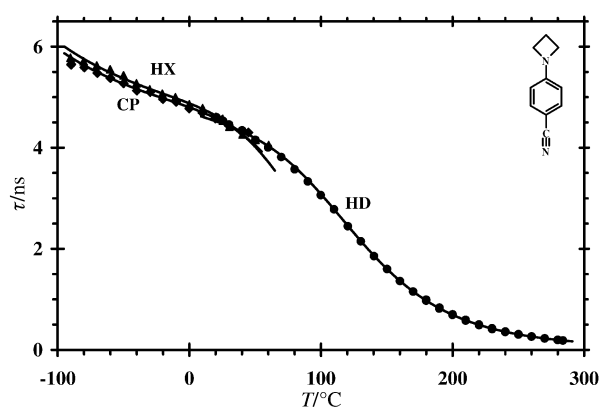
**Fig. 9** Plots of the fluorescence decay times  $\tau$  of P4CF3 in CP, HX and HD as a function of temperature. The lines through the data points represent the fitting resulting from the procedure described in the text (eqn. (1) and (2)).

reasonable agreement with those found in the two other solvents, see Table 3.

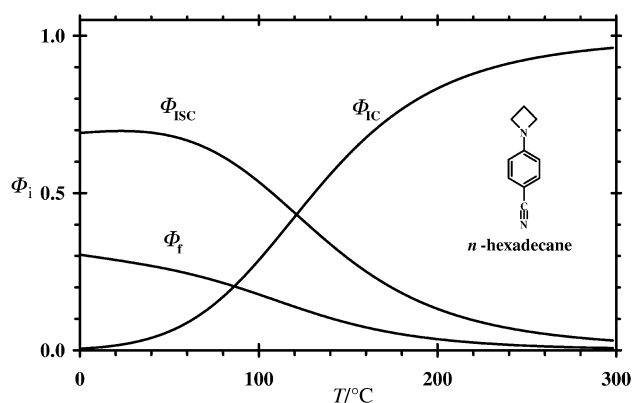
#### P4C. Fluorescence decay times in cyclopentane, n-hexane and n-hexadecane as a function of temperature

The temperature dependences of the fluorescence decay times  $\tau$  of P4C in cyclopentane, n-hexane and n-hexadecane are shown in Fig. 10. The decay times at 25 °C are all around 4.5 ns in the three solvents (Table 3), indicating that IC is not an important deactivation process for  $S_1$  at this temperature.

**P4C in n-hexadecane.** Only in the case of n-hexadecane is an appreciable decrease of  $\tau$  with increasing temperature observed for P4C, from 4.52 ns at 20 °C to 0.185 ns at 284 °C. This set of decay times, together with  $\Phi_f = 0.285$  (at 25 °C), was fitted by using eqn. (1) (with  $k_f \sim n^3$ ), see previous sections. The following results were obtained:  $E_{IC} = 38.5$  kJ mol<sup>-1</sup>,  $k_{IC}^0 = 21 \times 10^{12}$  s<sup>-1</sup>,  $E_{ISC} = 2.1$  kJ mol<sup>-1</sup>,  $k_{ISC}^0 = 0.4 \times 10^9$  s<sup>-1</sup> and  $k_f(0) = 2.1 \times 10^7$  s<sup>-1</sup>. From these parameters, the three yields  $\Phi_{IC}$ ,  $\Phi_{ISC}$  and  $\Phi_f$  can be calculated, see Fig. 11 and Table 4. It follows that  $\Phi_{IC}$  rises sharply with increasing temperature, from 0.01 at 25 °C to 0.95 at 284 °C. This increase in  $\Phi_{IC}$  leads to a decrease in  $\Phi_{ISC}$  as well as in  $\Phi_f$  when the temperature increases, from 0.70 to 0.04 ( $\Phi_{ISC}$ ) and from 0.29 to 0.01 ( $\Phi_f$ ) between 20 and 284 °C.



**Fig. 10** Plots of the fluorescence decay times  $\tau$  of P4C in CP, HX and HD as a function of temperature. The lines through the data points represent the fitting resulting from the procedure described in the text (eqn. (1) and (2)).



**Fig. 11** Temperature dependence of the internal conversion yield  $\Phi_{IC}$ , the intersystem crossing yield  $\Phi_{ISC}$  and the fluorescence quantum yield  $\Phi_f$  of P4C in HD. See text.

**P4C in cyclopentane and n-hexane.** With P4C in cyclopentane and n-hexane, the relatively small temperature dependence of  $\tau$ , only decreasing from 5.78 ns at -90 °C to 4.05 ns at 60 °C in n-hexane (Fig. 10), does not allow a sufficiently accurate determination of the IC rate parameters. Therefore, the value obtained for  $E_{IC}$  in n-hexadecane (38.5 kJ mol<sup>-1</sup>) was kept constant during the fitting procedure of the decay times in cyclopentane and n-hexane, giving the following results:  $k_{IC}^0 = 41 \times 10^{12}$  s<sup>-1</sup> (cyclopentane) and  $59 \times 10^{12}$  s<sup>-1</sup> (n-hexane), whereas  $E_{ISC} = 1.5$  kJ mol<sup>-1</sup>,  $k_{ISC}^0 = 0.3 \times 10^9$  s<sup>-1</sup> and  $k_f(0) = 2.2 \times 10^7$  s<sup>-1</sup> for both cyclopentane and n-hexane. When using the value of 1.5 kJ mol<sup>-1</sup> so obtained for  $E_{ISC}$  as a fixed parameter also in the fitting of the data for P4C in n-hexadecane, a slightly different set of data is obtained, see Table 3. The results of fixing the new value for  $E_{IC}$  (38.1 kJ mol<sup>-1</sup>) in fitting the P4C data in cyclopentane and n-hexane are also listed in Table 3. Fitting the experimental data of P4C in n-hexadecane with eqn. (1) and  $k_f \sim n^2$  does not lead to a significant change in the results, as was found for P4CF2 and P4CF3, see Table 3.

Based on the results obtained here it is seen that IC is negligible for P4C in cyclopentane and n-hexane at temperatures below 0 °C. By fitting the decay times of P4C over this temperature range (see Fig. 10), a value of 1.5 kJ mol<sup>-1</sup> was determined for  $E_{ISC}$  in cyclopentane and n-hexane, in agreement with the results obtained above by fixing  $E_{IC}$  (Table 3).

#### Different IC efficiencies of P4CF2, P4CF3 and P4C

The increase in IC efficiency for the series P4C, P4CF3, P4CF2 in alkane solvents is caused by a decrease in  $E_{IC}$ , with the values (in cyclopentane) 38.1 kJ mol<sup>-1</sup> (P4C), 19.3 kJ mol<sup>-1</sup> (P4CF3) and 12.6 kJ mol<sup>-1</sup> (P4CF2), see Table 3. The large IC barrier for P4C explains that IC with this molecule in alkane solvents only becomes an important decay channel above room temperature. Because the IC activation energies  $E_{IC}$  of the molecules P4CF<sub>x</sub> are considerably larger than those of ISC, see Table 3, IC becomes the dominant deactivation process for  $S_1$  at higher temperatures, as shown in Fig. 8 and 11.

The shortening of the fluorescence decay time  $\tau$  in cyclopentane at 25 °C of P4CF2 (0.137 ns) and P4CF3 (0.846 ns) as compared with P4C (4.55 ns), is mainly caused by IC ( $k_{IC}$ :  $6.5 \times 10^9$  s<sup>-1</sup> (P4CF2),  $0.39 \times 10^9$  s<sup>-1</sup> (P4CF3) and  $0.01 \times 10^9$  s<sup>-1</sup> (P4C)) as well as by a more efficient ISC:  $k_{ISC} = 0.37 \times 10^9$  s<sup>-1</sup> (P4CF2) and  $0.61 \times 10^9$  s<sup>-1</sup> (P4CF3) against  $0.15 \times 10^9$  s<sup>-1</sup> (P4C). Also the radiative rate constants  $k_f$  of P4CF2 ( $12 \times 10^7$  s<sup>-1</sup>) and P4CF3 ( $13 \times 10^7$  s<sup>-1</sup>) are larger than that of P4C ( $6 \times 10^7$  s<sup>-1</sup>), see Table 4 (cyclopentane), probably due to the mixing of the  $S_2(^1L_a)$  and  $S_1(^1L_b)$  states of P4C, caused by the molecular asymmetry introduced by the F-substituents.

#### Mechanism of internal conversion

The occurrence of efficient internal conversion from  $S_1$  to  $S_0$  taking place in the molecules P4CF<sub>x</sub> in alkane solvents indicates that the energy gap  $\Delta E(S_1, S_0)$  between these two states can become considerably smaller than the energy  $E(S_1)$  of the  $S_1$  state reached by absorption from the equilibrated ground state. Under these conditions, fast IC can take place, as described by the energy gap law.<sup>31,33-35</sup> The observed activation energies  $E_{IC}$  would then be the barriers for a thermally activated configurational change in  $S_1$  that can bring the molecules P4CF<sub>x</sub> in a configuration which is energetically strongly unfavourable in the ground state as compared to  $S_1$  and hence leads to a smaller energy gap  $\Delta E(S_1, S_0)$ . The influence of the presence and position of the F-substituent in the phenyl ring of the P4CF<sub>x</sub> molecules shows that the differences in the electron density distribution of the  $S_1$  and  $S_0$  states brought about by excitation, play an important role in determining the magnitude of the  $E_{IC}$  barrier. As seen from the absorption spectra (Fig. 1), the



compound P4CF2 with the smallest IC barrier has the largest energy gap between  $S_2$  and  $S_1$ , which means that  $\Delta E(S_2, S_1)$  does not exert a significant influence on the IC process in the P4CFx molecules. This is different from what has been concluded for 1-aminonaphthalenes<sup>9,12–16</sup> and for the ICT reaction in aminobenzonitriles.<sup>3–5,8,29,36</sup> There is no experimental indication that for the P4CFx systems a conical intersection, as postulated in other cases,<sup>14,15</sup> is present on the deactivation pathway from  $S_1$  to  $S_0$ .

## Conclusion

The introduction of a fluoro-substituent into the phenyl ring of P4C leads for the molecules P4CF2 and P4CF3 to a decrease in the fluorescence quantum yield and a shortening of the fluorescence decay time in alkane solvents. There is no indication of dual emission in the fluorescence spectra of the P4CFx molecules in the alkane solvents and the fluorescence decays are accordingly single exponential over the entire temperature range investigated. As deduced from the measurement of ISC yields, internal conversion is strongly enhanced by F-substitution. The IC efficiency is larger for P4CF2 than for P4CF3, which is due to a smaller activation energy  $E_{IC}$ : 12.6 kJ mol<sup>-1</sup> (P4CF2) as compared with 19.3 kJ mol<sup>-1</sup> (P4CF3). Although IC is practically absent for P4C in these solvents at room temperature, it becomes the dominant  $S_1$  decay channel for temperatures higher than 120 °C in n-hexadecane, a consequence of its large IC activation energy of 38.1 kJ mol<sup>-1</sup>.

It is assumed that the reduction of  $E_{IC}$  by F-substitution in P4CF2 and P4CF3 is caused by a change in the electron distribution in these molecules upon excitation. This change may lower the barrier to reach an  $S_1$  configuration of the P4CFx molecules, which is energetically strongly unfavourable in the ground state as compared to  $S_1$ , thereby reducing the energy gap  $\Delta E(S_1, S_0)$  and opening up a thermally activated IC decay channel.

The activation energies  $E_{ISC}$  of the P4CFx compounds have values around 1 kJ mol<sup>-1</sup>, considerably lower than the IC barriers (see above), which explains why IC becomes the main radiationless process at sufficiently high temperatures. The preexponential factors  $k_{ISC}^0$ , between  $0.3 \times 10^9$  and  $1 \times 10^9$  s<sup>-1</sup>, are more than three orders of magnitude smaller than their IC counterparts  $k_{IC}^0$ , which supports the spin-forbidden character of the decay channel identified as ISC. The radiative rate constant  $k_f$  of P4CF2 and P4CF3 is about two times larger than that of P4C, which is attributed to the mixing of the  $S_1(^1L_b)$  and  $S_2(^1L_a, CT)$  states caused by the molecular asymmetry introduced by the F-substituents.

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