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Absorption and fluorescence of 1-(2-pyridyl)-piperazine and four diisocyanate derivatives in solution

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Abstract

Airborne diisocyantes can be determined by fluorimetry after sampling and derivatization to stable urea derivatives using 1-(2-pyridyl)-piperazine (2PP) as reagent. Because the photophysical properties of the 2PP-diisocyanate derivatives are still unknown, the absorption and fluorescence behaviour as well as their changes under the influence of heat or irradiation have been investigated in various solvents. From solvent dependent measurement an increase in the dipole moment upon excitation was evident for 2PP. The urea derivatives exhibit a fluorescence $\phi_f = 0.14$–0.21 at 20 °C, which was found to be strongly dependent on temperature in all cases. The activation energies E_A were determined according to an Arrhenius-type relationship. All urea compounds were stable in methanolic solution for more than 200 h under exposure to heat (60 °C) or daylight. © 1997 Elsevier Science S.A.

Keywords: Pyridyl-piperazines; Diisocyanates; Absorbance; Fluorescence; Degradation

1. Introduction

Diisocyanates are an important class of chemicals with commercial interest, which are frequently used in the manufacture of indoor materials like adhesives, coatings, foams and rubbers [1,2]. In some types of particleboard, the diisocyanates have substituted formaldehyde [3]. Isocyanates are characterized by the electrophilic –N=C=O group, which may easily react with molecules containing "active" hydrogen, such as water or alcohols. On hydrolysis with water primary amines are formed (Eq. (1)),

$$R\text{–}N{=}C{=}O + H_2O \rightarrow R\text{–}NH_2 + CO_2 \qquad (1)$$

$$R\text{–}N{=}C{=}O + R'-OH \rightarrow R\text{–}NH\text{–}CO\text{–}O\text{–}R' \qquad (2)$$

while a reaction with alcohols leads to carbamates (urethanes) (Eq. (2)). Polyurethane (PUR) products are then obtained from a polyaddition of diisocyanate and diol components. Commonly industrial applied compounds are 2,6-toluene-diisocyanate (2,6-TDI), 2,4-toluene-diisocyanate (2,4-TDI), 4,4′-diphenylmethane-diisocyante (MDI) and hexamethylene-diisocyanate (HDI) (see Fig. 1). The diisocyanate monomers are known as respiratory sensitizers and cause irritation of eyes, skin and mucous membrane. Therefore it is desired to measure even trace quantities in the atmosphere of workplace environments or private dwellings. However, the accurate determination of airborne diisocyanates is a sophisticated procedure owing to their high reactivity and low concentration levels, which are in the magnitude of ng m^{-3}.

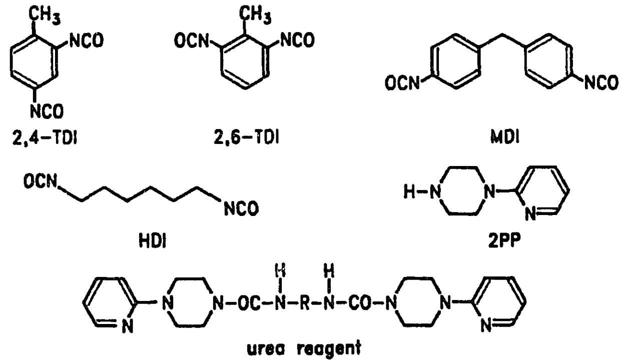

Fig. 1. Chemical structures of 2,6-TDI, 2,4-TDI, HDI, MDI, 2PP and the resulting urea compounds.

On sampling, an immediate derivatization to stable compounds is necessary and a number of different procedures have been published [4,5]. A standard colorimetric method was introduced by Marcali [6] and later modified [7,8]. More sensitive techniques use gas chromatography [9] or HPLC with UV, fluorescence or electrochemical detection [10–17]. The current state of the art involves the use of

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piperazine compounds which react with diisocyanates to form electrochemically detectable or fluorescent urea derivatives [18–23]. Two OSHA methods [24,25] describe a derivatization with 1-(2-pyridyl)-piperazine (2PP) to 1,6-bis-(4-(2-pyridyl)-1-piperazine-carbamyl)-hexane (HDI-2PP), 2,6-bis-(4-(2-pyridyl)-1-piperazine-carbamyl)-toluene (2,6-TDI-2PP), 2,4-bis-(4-(2-pyridyl)-1-piperazine-carbamyl)-toluene (2,4-TDI-2PP) and *N,N'*-(methylenediphenylene)-bis-4-(2-pyridinyl)-1-piperazine-carboxamide (MDI-2PP) (see Fig. 1) on a coated filter, using the combination HPLC/fluorescence for separation and detection, respectively.

Although the utilities (sampling devices) for this analytical procedure are now commercially distributed [26], there is little information about the spectroscopic properties of the resulting urea reagents [27]. Nevertheless, knowledge about any changes in the absorption and fluorescence spectra on exposure of light or heat is of special importance for analytical purposes. Therefore this work was carried out with the aim of enlarging the scope of spectroscopic properties of the four important fluorescent urea compounds. In particular, thermal effects on the absorption and fluorescence spectra as well as the thermal and photochemical degradation have been investigated. The results reported here are helpful to improve the sensitivity of a HPLC/fluorescence method for the detection of airborne diisocyanates.

2. Materials and methods

2,6-TDI (Fluka, CAS #91-08-7), 2,4-TDI (Fluka, CAS #584-84-9), MDI (Aldrich, CAS #101-68-8), HDI (Aldrich, CAS #822-06-0) and 2PP (Aldrich, CAS #34803-66-2) were used as received. Methanol (MeOH) and acetonitrile (ACN) (Merck) were of spectroscopic grade. Toluene was redistilled and dried subsequently to remove traces of water. *p*-Terphenyl (Aldrich, CAS #92-94-4) was purified by recrystallization. For the preparation of each urea compound, 1.5 g 2PP were solved in 20 ml toluene. Stoichiometric portions of the diisocyanate suspended in 15 ml toluene (0.25 g MDI, 0.16 g HDI, 0.17 g 2,6-TDI or 0.17 g 2,4-TDI) were added. After stirring for 1 h at 30 °C the precipitate was sucked on a glass-fibre filter and washed with toluene and diethyl ether. Then the product was dried at 30 °C in a vacuum cabinet until constancy of weight.

The UV/VIS spectra were recorded on a Perkin-Elmer Lambda 17 spectrometer. Fluorescence spectra were measured on a quantum-corrected spectrofluorimeter (Perkin-Elmer MPF-44E). Both instruments were connected to personal computers for controlling and digital data recording. The areas under the spectra were determined by numerical integration.

For temperature control, the samples were placed in special cuvette holders in Dewar vessels and were heated by circulating water from a constant-temperature bath. The temperature was measured at the samples by a resistance temperature detector (Newport 267) and from 10 °C to 60 °C the stability was about 1 °C. The maxima of the spectra were determined by fitting the top of the curve with a gaussian function and calculating the peak value of the fit curve.

The fluorescence decay function of 2,6-TDI-2PP was measured at 20 °C in a 1 cm × 1 cm cuvette, employing the technique of time-correlated single photon counting (TCSPC) as described elsewhere [28]. Fluorescence quantum yields ϕ_f were determined from quantum corrected spectra using a degassed sample of *p*-terphenyl in cyclohexane ($\phi_f(20\,°C) = 0.93$) [29] as standard.

3. Spectroscopic properties

The absorption spectra of 2,6-TDI-2PP, 2,4-TDI-2PP, HDI-2PP and MDI-2PP in methanolic solution are shown in Fig. 2. All spectra are similar in shape with broad and unstructured maxima at 248–252 nm and 295–305 nm. From a comparison with 2PP (see Fig. 3) it is evident that absorption in this spectral range stems from the piperazine–pyridine fragment. Substitution of the proton, which bonded to the nitrogen atom of the piperazine ring in the 4 position, causes no spectral shifts. However, the absorption coefficients of the sub-

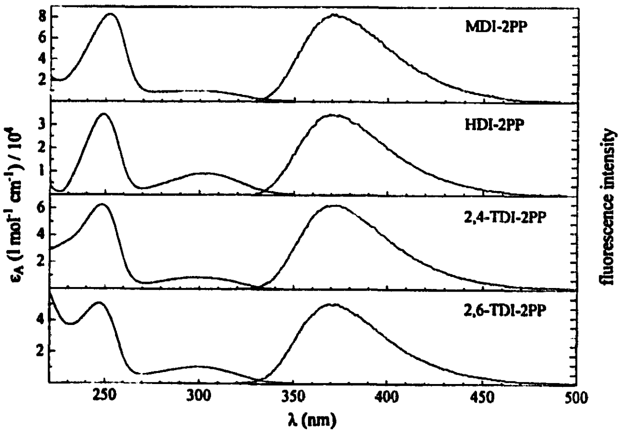

Fig. 2. Absorption and fluorescence spectra of 2,6-TDI-2PP, 2,4-TDI-2PP, HDI-2PP and MDI-2PP in methanolic solution.

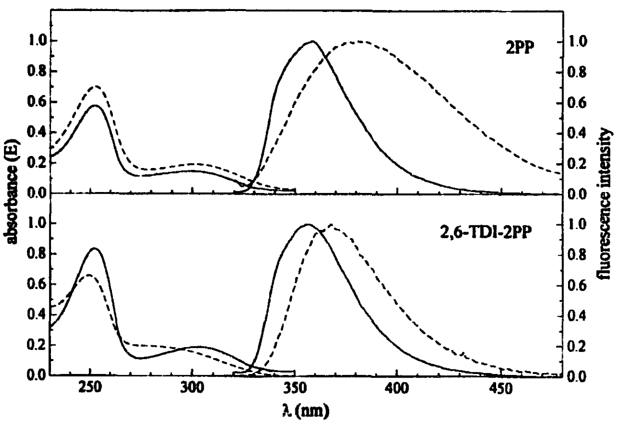

Fig. 3. Absorption and fluorescence spectra of 2PP and 2,6-TDI-2PP in *n*-hexane (———) and acetonitrile (— — —).

Table 1
Photophysical properties of 2,6-TDI-2PP, 2,4-TDI-2PP, HDI-2PP, MDI-2PP and 2PP (n.d. = not determined). All parameters were determined in methanolic solution

Parameter	2,6-TDI-2PP	2,4-TDI-2PP	HDI-2PP	MDI-2PP	2PP
Solvent	MeOH	MeOH	MeOH	MeOH	MeOH
λ_{ex}^{max} (S_3, $\pi\pi^*$) (nm)	248	249	249	252	246
λ_{ex}^{max} (S_1, $\pi\pi^*$) (nm)	304	293	303	302	302
λ_{em}^{max} (nm)	369	370	371	371	382
ϵ_{ex}^{max} (S_3) (l mol^{-1} cm^{-1})	50 720	62 383	34 433	82 880	7374
ϕ_f (20 °C)	0.21	0.18	0.14	0.14	≤0.01
τ (ns) (20 °C)	4.2	n.d.	n.d.	n.d.	n.d.
E_A (kJ mol^{-1})	6.6	5.7	8.4	10.4	n.d.

stituted 2PP derivatives are distinctly higher. Molar absorption coefficients were determined in methanol from linear concentration vs. absorbance curves. The results, which are in accordance with data of Hardy and Walker [27] measured in DMSO, are given in Table 1.

The lowest excited singlet state (S_1) of 2PP and the investigated derivatives of 2PP is of $\pi\pi^*$ type. The S_2, which should result from a weak $n\pi^*$ transition of the nitrogen non-bonding electrons [30], was not visible, because a strong $S_3(\pi\pi^*)$ transition overlaps. The absorption maximum of the $S_3(\pi\pi^*)$ transition of 2PP in acetonitrile is located at 250 nm (40 000 cm^{-1}) with 7374 1 mol^{-1} cm^{-1}. The $S_1(\pi\pi^*)$ transition of 2PP has a maximum at 302 nm (33 113 cm^{-1}) with 2020 1 mol^{-1} cm^{-1} (see Fig. 3). For the determination of oscillator strengths the absorption spectrum was fitted by nonlinear regression to a sum of two gaussians $\epsilon(\tilde{\nu}) = \sum_{i=1}^{2} a_{1i} \exp(-(\tilde{\nu} - a_{2i})^2/2a_{3i}^2)$. $f(S_3) = 0.135$ and $f(S_1) = 0.046$ were then obtained from the well-known equation $f = 4.319\int\epsilon(\tilde{\nu})\,d\tilde{\nu}$ [31]. A theoretical treatment of the 2PP transitions yielded 31 450 cm^{-1} with $f = 0.017$ for the $S_1(\pi\pi^*)$, 41 600 cm^{-1} with $f = 0.002$ for the $S_2(n\pi^*)$ and 41 600 cm^{-1} with $f = 0.169$ for the S_3 ($\pi\pi^*$). The calculated dipole moment of 2PP in the ground state is about 2.75 D [32].

The fluorescence spectra of 2,6-TDI-2PP, 2,4-TDI-2PP, HDI-2PP and MDI-2PP in methanol are also shown in Fig. 2. In Fig. 3, the absorption and fluorescence spectra of 2PP and 2,6-TDI-2PP in *n*-hexane and acetonitrile are presented. It is obvious, that the solvent polarity causes no solvatochromic shift effect [33] on the absorption of 2PP. For 2,6-TDI-2PP, the absorption is slightly blue shifted in the non-polar *n*-hexane. In all cases the fluorescence is broad and unstructured, a large Stokes shift of about 70 nm is obvious. The fluorescence spectra show a bathochromic shift with increasing solvent polarity. This effect is stronger for 2PP with 356 nm (*n*-hexane) → 382 nm (acetonitrile) than for 2,6-TDI-2PP with 355 nm (*n*-hexane) → 369 nm (acetonitrile). Absorption and fluorescence spectra were also measured in different aprotic solvents [34] in order to determine the charge separation, which might be caused by charge-transfer interaction between the pyridine ring and the conjugating nitrogen atom of the piperazine ring, from the solvent polarity function as described by Lippert [35],

$$\Delta\tilde{\nu} = \frac{2(\Delta\mu)^2}{hca^3} f(D) \qquad (3)$$

$$f(D) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n_B^2 - 1}{2n_B^2 + 1} \qquad (4)$$

where the difference of absorption and fluorescence maximum wavenumbers (Stokes shift) $\Delta\tilde{\nu} = \tilde{\nu}_{ex} - \tilde{\nu}_{em}$ is plotted against $f(D)$. Here h is the Planck constant, n_B is the refractive index of the solvent and c is the velocity of light. From the slope of Eq. (3), the change in the dipole moment $\Delta\mu = \mu_{ex} - \mu_g$ upon excitation can be determined. The cavity radius a was obtained from summation of the van der Waals increments by applying the method of Edward [36]. With $a = 3.4$ Å and a slope of 6268 ± 400 cm^{-1}, $\Delta\mu = 4.9$ D resulted for 2PP, which corresponds to a charge separation of about 1 Å.

The spectral shifts of the 2PP-diisocyanate derivatives were too small to obtain a clear linear correlation with Eq. (3). The absorption and fluorescence spectra of 2,6-TDI-2PP in acetonitrile, acetone and some aliphatic alcohols (methanol → *n*-octanol) were almost identical (plots not shown). A different behaviour could be observed in a 50:50 mixture of acetonitrile/water, which is a common solvent system for HPLC. Here, the fluorescence was red shifted to 380 nm with a strongly reduced intensity, which might result from solute–solvent interactions, such as hydrogen bonding.

The absorption and fluorescence behaviour of 2PP and derivatives show a great similarity to 2-pyridinamine [37–40]. However, the addition of small amounts of ethanol to a dilute solution of 2-pyridinamine in isooctane caused shape and intensity effects on the spectra. This was attributed to formation of a hydrogen bonded 1:1 complex between 2-pyridinamine and ethanol [38]. Analogous complex formation was not evident for 2PP. This might be mainly due to a steric hinderance, caused by the more voluminous piperazine ring. As expected, the absorption spectra were strongly perturbed when the pH value was decreased and it is shown for 2,6-TDI-2PP in Fig. 4, that a new absorption band appears at 275 nm. 2PP and the isocyanate derivatives are of weak basicity. In comparison to pyridine with $pK_a = 5.23$, the nucleophility of the heterocyclic nitrogen atom, where protonation will take place, is enhanced by the +M effect of the pipera-

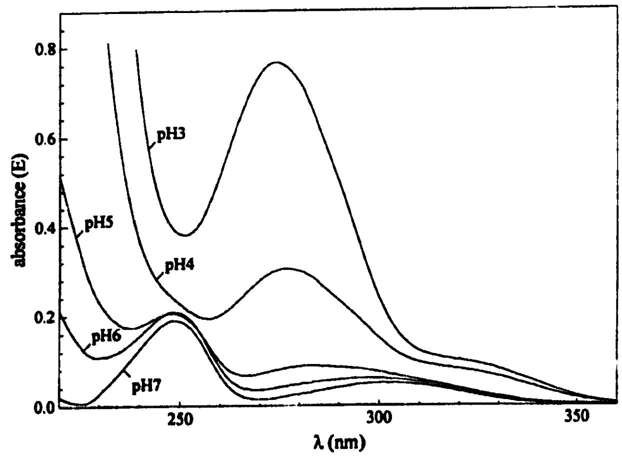

Fig. 4. Influence of the pH value on absorption spectra of 2,6-TDI-2PP in methanolic solution.

zine group (–NR$_2$). The pK_a values were not exactly determined but should be in the magnitude of 2-aminopyridine (pK_a=6.86) and 2-dimethylaminopyridine (pK_a=7.0) [41].

The experimental fluorescence lifetime of a non-degassed 2,6-TDI-2PP sample in methanol at room temperature is $\tau_0(293\ \mathrm{K}) = 4.2$ ns ($\chi^2 = 1.02$, single exponential fit). Fluorescence quantum yields ϕ_f at 20 °C were obtained from stationary fluorescence measurements relative to *p*-terphenyl by use of Eq. (3) [42]. All samples were excited in the maximum of the S$_1$ transition, because the intensity of a xenon lamp drops sharply below 290 nm.

$$\phi_f = \phi_f^{\mathrm{ref}} \frac{F}{F^{\mathrm{ref}}} \left(\frac{n_B^2}{(n_B^{\mathrm{ref}})^2} \right) \frac{1-10^{-E^{\mathrm{ref}}_{\lambda_{ex}}}}{1-10^{-E_{\lambda_{ex}}}} \tag{5}$$

F and F^{ref} are the areas under the fluorescence spectra, E and E^{ref} are the absorbances at the excitation wavelength λ_{ex} of sample and reference, respectively. n_B is the refractive index of the solvent. The results are given in Table 1. We did not determine experimental errors but approximate uncertainties of about ±0.05. All diisocyanate-2PP derivatives exhibit fluorescence with quantum yields ranging from 0.14 to 0.21 in methanol. No significant differences were observed for ϕ_f in the solvent acetonitrile. This makes these compounds very suitable for a sensitive analytical fluorescence monitoring after separation via HPLC with a significantly improved detection limit. The fluorescence quantum yield of 2PP was well below 0.01 in methanol and acetonitrile.

4. Temperature dependence of fluorescence

A quantification of diisocyanates can also be performed by measuring the absorption of the 2PP derivatives after separation by HPLC. However, many solvents and impurities show absorption in the wavelength range 200–300 nm, resulting in low signal-to-noise ratios and low detection limits. Owing to the fluorescence response (see above), the fluorimetric monitoring is much more sensitive, but it is well known that the fluoresescence quantum yield depends strongly on temperature. As a consequence, the effects of temperature on the fluorescence quantum yields must be known if the method is applied.

In the absence of photochemical reactions, the non-radiative pathways available for singlet deactivation of an excited state in competition to fluorescence are intersystem crossing (isc) and internal conversion (ic.). With $k_d = k_{isc} + k_{ic}$, the fluorescence quantum yield is defined by $\phi_f = k_f/(k_f + k_d)$, which gives

$$k_d = k_f \left(\frac{1}{\phi_f} - 1 \right) \tag{6}$$

With Eq. (6) the temperature dependence of ϕ_f can be expressed by an Arrhenius-type relationship:

$$\ln\left(\frac{1}{\phi_f} - 1 \right) = \frac{-E_A}{RT} + \ln\left(\frac{A}{k_f} \right) \tag{7}$$

The temperature dependence was studied in dilute and non-degassed methanolic solutions. Each sample was heated from 10 °C to 60 °C and then cooled again to 10 °C while ϕ_f was measured in 10 °C steps. This procedure was performed twice and in the short time range of the investigation (5 h) the fluorescence response was fully reversible.

The temperature dependences of ϕ_f are depicted in Fig. 5. The E_A values obtained from linear regression fits (see Eq. (7)) are summarized in Table 1. The statistical errors were in the range of 1–2 kJ mol^{-1}, which makes a quantitative discussion difficult. Nevertheless, it can be said that for HDI-2PP (8.4 kJ mol^{-1}) and MDI-2PP (10.4 kJ mol^{-1}) the E_A values are significantly higher than those derived for 2,6-TDI-2PP (6.6 kJ mol^{-1}) and 2,4-TDI-2PP (5.7 kJ mol^{-1}). The results demonstrate the strong dependence of the fluorescence quantum yield on temperature. For MDI-2PP and HDI-2PP we observed a decrease of about 10% in ϕ_f when the temperature was increased from 20 °C to 30 °C. Therefore, care has to be taken if diisocyanates are quantified by

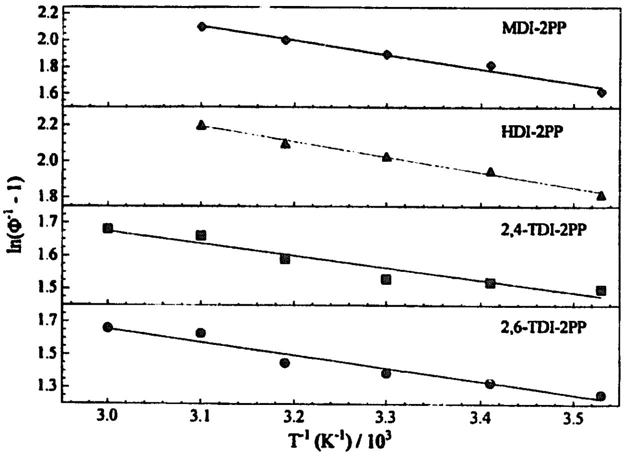

Fig. 5. Arrhenius plots (see Eq. (7)) of temperature dependent ϕ_f measurements of 2,6-TDI 2PP, 2,4-TDI-2PP, HDI-2PP and MDI-2PP in methanolic solution.

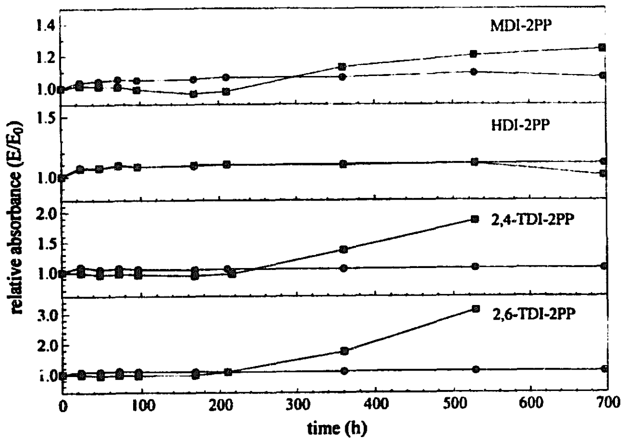

Fig. 6. Thermal stability of 2,6-TDI-2PP, 2,4-TDI-2PP, HDI-2PP and MDI-2PP at 20 °C (●) and 60 °C (■) in methanolic solution.

fluorimetry of the 2PP derivatives and a constant temperature is absolutely necessary for calibration and measurement.

5. Degradation of 2PP derivatives

The thermal degradation effects of 2PP derivatives were studied as a function of time in methanolic solution. Dilute samples ($E \approx 0.5$) were prepared and stored in the dark at 20 °C and 60 °C for a period of 700 h, respectively. The results are shown in Fig. 6. For each compound the absorbance E was monitored in the maximum of the S_3 transition and normalized to E/E_0 for better comparison. At 20 °C all 2PP derivatives were stable and no significant deviations from the initial absorbance E_0 were evident. HDI-2PP was also stable at 60 °C. A slight effect could be observed for MDI-2PP. 2,4-TDI-2PP and 2,6-TDI-2PP were stable for about 200 h at 60 °C. Then the absorbances increased rapidly, indicating a starting degradation process.

To investigate a possible photochemical decomposition, dilute samples of all urea derivatives were exposed to daylight for 700 h at 20 °C. For HDI-2PP, MDI-2PP and 2,4-TDI-2PP there was no measurable effect (plot not shown). Only for 2,6-TDI-2PP, did E/E_0 increase to 1.17 within 700 h.

6. Conclusions

The photophysical properties of 2PP and four urea derivatives formed with the diisocyantes 2,6-TDI-2PP, 2,4-TDI-2PP, HDI and MDI have been investigated in solution. All urea compounds show high molar absorption coefficients and are fluorescent with quantum yields $\phi_f = 0.14–0.21$ at room temperature. The solvatochromic effect on absorption and fluorescence spectra is small. Deactivation via non-radiative processes was found to be strongly dependent on temperature. At 60 °C, methanolic solutions of the urea derivatives are stable for more than 200 h when kept in the dark. This is of importance for practical purposes because collected samples can be stored for several days and must not be analysed immediately. The results obtained in this work confirm that 2,6-TDI-2PP, 2,4-TDI-2PP, 2PP-HDI and 2PP-MDI are well suitable for the sensitive fluorimetric determination of the corresponding diisocyanates. Because of the low selectivity of the method and similarity of the spectra, a chromatographic separation, preferably via HPLC, is necessary. This procedure will also remove possible contaminants and reduce undesired quenching effects. When using 2PP-impregnated cartridges according to modified OSHA methods no. 42 and 47 [24,25] and applying HPLC/fluorescence, detection limits for airborne HDI, MDI, 2,4-TDI and 2,6-TDI below 10 ng m^{-3} could be obtained. Analytical details will be described in a forthcoming paper.

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