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# Fluorescence Quenching and Laser Photolysis of Dipyrrolylbenzenes in the Presence of Chloromethanes<sup>1</sup>

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**Abstract** — Fluorescence quenching of 1,4-bis(1*H*-pyrrol-1-yl)benzene, 1-(1*H*-pyrrol-2-yl)-1-(1-vinyl-1*H*-pyrrol-1-yl)benzene, and 1,4-bis(1-vinyl-1*H*-pyrrol-2-yl)benzene with chloromethanes (methylene chloride, chloroform, and carbon tetrachloride) in solvents with different polarities follows electron-transfer mechanism. The occurrence of an electron-transfer step is confirmed by formation of short-lived pyrrolylbenzene radical cations. An exception is quenching of fluorescence of 1,4-bis(1-vinyl-1*H*-pyrrol-2-yl)benzene in *n*-hexane in the presence of CCl<sub>4</sub> and CHCl<sub>3</sub> and in pure CCl<sub>4</sub>. In this case, neutral 1,4-bis(1-vinyl-1*H*-pyrrol-2-yl)benzene radical cation and chloride anion. A relation was found between the nature of the short-lived species detected by laser photolysis and stable product obtained by stationary photolysis. **DOI:** 10.1134/S1070363207080166

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Fluorescent dipyrroles in which electron-donor pyrrole rings are linked through an aromatic or other electron-acceptor bridge attract interest as precursors of extended  $\pi$  systems that are widely used in the field of optical technologies (as sensors, optical switchers, light-emitting diods, semiconductors with a narrow band gap, molecular crystals for frequency transduction) [1–5]. Due to their high hyperpolarizability ( $\beta$ ), 1,4-bis(1*H*-pyrrol-2-yl)benzenes and their analogs are also promising as materials for computing and signalprocessing devices operating in the optical frequency range [6]. Optical and electrical parameters of materials are largely determined by dynamics of excited states of monomeric units, their ability to generate charged species, and properties of radical cations.

In the present study we used model 1,4-bis(1*H*-pyrrol-2-yl)benzenes to elucidate mechanism of the reaction between photochemically excited pyrroles and electron-acceptor molecules. For this purpose, we examined electronic absorption and luminescence spectra of 1,4-bis(1*H*-pyrrol-2-yl)benzene (**I**), 1-(1*H*-pyrrol-2-yl)-4-(1-vinyl-1*H*-pyrrol-2-yl)benzene (**II**), and 1,4-bis(1-vinyl-1*H*-pyrrol-2-yl)benzene (**III**) (di-

pyrrolylbenzenes), mechanism of their fluorescence quenching with chloromethanes  $(CH_2Cl_2, CHCl_3, CCl_4)$ , and effect of the medium on the nature and spectral properties of short-lived intermediates generated in the above systems by nanosecond laser photolysis (NLP).

**Synthesis of dipyrrolylbenzenes.** 1,4-Bis(1*H*-pyrrol-2-yl)benzene (**I**) and its substituted derivatives were synthesized previously according to laborious multistep procedures [5–7] in an overall yield of 10 [7] or 20% [5], by the Negishi cross coupling of protected *N*-(trimethylsilyl)ethoxymethylpyrrole with 1,4-dibromobenzene in the presence of NiCl<sub>2</sub>dppp as catalyst [5], or by cyclization of N,N'-diallylterephthalimidoyl dichloride by the action of *t*-BuOK in THF/DMF [7]. On the other hand, ten years ago we reported [8–10] on one-pot synthesis of 1,4-bis(1-vinyl-1*H*-pyrrol-2-yl)benzene (**III**) in 30% yield from 1,4-diacetylbenzene dioxime and acetylene (Trofimov reaction [11]), and methods for deprotection of *N*-vinylpyrroles were developed [12, 13].

In the present work we synthesized dipyrrolylbenzenes **I–III** according to a modified Trofimov procedure with the use of 1,4-diacetylbenzene dioxime cesium salt. In such a way we succeeded in obtaining three target products **I–III** in an overall yield of 28.6% in one preparative step (Scheme 1).

<sup>&</sup>lt;sup>1</sup> Dedicated to M.G. Voronkov on the 85th anniversary of his birth.



1,4-Bis(1H-pyrrol-2-yl)benzene (I) was prepared in 83% yield by deprotection of divinyl derivative III via successive treatment with  $Hg(OAc)_2$  and  $NaBH_4$  according to improved procedure [12, 13] (Scheme 2).



Electronic absorption and luminescence spectra of compounds I–III. The long-wave absorption band in the electronic absorption spectra of compounds I– III is displaced toward shorter wavelengths in going from I to II and then to III (Fig. 1, Table 1). Simultaneously, its intensity decreases. Most probably, this is the result of weakening of conjugation in the system due to increase in dihedral angles between the benzene ring and initially one and then two pyrrole rings upon successive replacement of hydrogen at the pyrrole nitrogen atoms by bulky vinyl groups.

The equilibrium structures of molecules **I–III** in the ground state, calculated by the B3LYP/6-3111G\* method, are shown in Fig. 2. For all compounds **I–III**, *trans* conformations of the pyrrole rings are preferred. The pyrrole rings decline from the benzene ring plane through a dihedral angle of  $28-29^{\circ}$  for unsubstituted dipyrrolylbenzene and  $43-45^{\circ}$  for *N*-vinylpyrrole fragments.

Unlike absorption spectra, the fluorescence maxima of compounds **I–III** are less sensitive to substitution. Introduction of vinyl groups makes the vibrational structure less resolved and reduces the fluorescence quantum yield ( $\Phi_f$ ) in going from compound **I** to **III** (Fig. 1, Table 1). The observed parallelism in the hypochromic effect in the absorption spectra and reduction of  $\Phi_f$  indicates that the main reason for the latter is increase in the radiative fluorescence lifetime  $(\tau_r)$  in the series **I–III**. Clearly defined vibrational structure in the fluorescence spectra of these compounds (which is most pronounced in *n*-hexane solutions) and the lack of vibrational structure in the absorption spectra (Fig. 1) are typical of nonrigid



**Fig. 1.** Electronic absorption and fluorescence spectra of dipyrrolylbenzenes **I–III** in acetonitrile. The intensities are proportional to the molar absorption coefficients in the absorption spectra and to the quantum yields in the fluorescence spectra. The intensities in the spectra of **I** are normalized by unity.

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**Fig. 2.** Equilibrium geometric structures of the ground states of molecules I–III, calculated by the B3LYP/6-311G\* method.

molecules; this pattern suggests flattening of molecules **I**-**III** upon excitation.

Fluorescence quenching of dipyrrolylbenzenes with chloromethanes. Addition of a small amount of  $CHCl_3$  or  $CCl_4$  to a solution of compound I–III in acetonitrile or hexane appreciably reduces its fluorescence intensity. Fluorescence quenching is not ac-

**Table 1.** Absorption and luminescence spectra of dipyrrolylbenzenes<sup>a</sup>

Comp. no.	Absorption		Fluorescence			
	λ <sub>max</sub> , nm	$^{\epsilon_{\max}}$ , l mol <sup>-1</sup> cm <sup>-1</sup>	λ <sub>max</sub> , nm	$\Phi_{\rm f}$		
Ι	328.4	40 000	377	1.00		
II	317.8	33 300	385	0.92		
III	307.3	23 300	383	0.70		
<i>n</i> -Hexane						
Ι	326.5	_	372	-		
II	314.8	_	376	_		
III	306.8		377			

<sup>a</sup> Insofar as compounds I–III are poorly soluble in *n*-hexane, the corresponding  $\varepsilon$  and  $\Phi_f$  values were not measured.



**Fig. 3.** Fluorescence spectra of  $2 \times 10^{-6}$  M solutions of compound **II** in *n*-hexane ( $\lambda_{\text{exc}} = 334$  nm) in the presence of CHCl<sub>3</sub>; concentration of CHCl<sub>3</sub>, M: (*I*) 0, (2) 0.12, (3) 0.25, (4) 0.38, and (5) 0.5.

companied by variation of the shape of emission bands or appearance of new bands in the long-wave region of the spectrum. As an example, Fig. 3 shows the fluorescence spectra of compound **II** in *n*-hexane at different concentrations of chloroform.

For all the examined compounds, the dependence of  $I_0/I$  on the concentration of CHCl<sub>3</sub> is linear and is well described by Stern–Volmer type Eq. (1).

$$I_0/I = 1 + K_d[CHCl_3].$$
 (1)

Here,  $I_0$  and I are the fluorescence intensities in the absence and in the presence of quencher, respectively. If quencher is carbon tetrachloride, the dependences of  $I_0/I$  versus [CCl<sub>4</sub>] for compounds **I**–**III** both in polar and in nonpolar solvents are nonlinear (Fig. 4); in the examined range of quencher concentrations, these dependences are well described by Eq. (2):

$$I_0/I = 1 + (K_d + K_x)[\text{CCl}_4] + K_d K_x[\text{CCl}_4]^2.$$
(2)

Methylene chloride weakly quenches fluorescence of compounds **I–III**. These compounds show fluorescence even when methylene chloride is used as solvent. By contrast, no fluorescence of dipyrrolylbenzenes **I–III** is observed in chloroform and carbon tetrachloride. The fluorescence quenching constants in methylene chloride were not determined on a quantitative level, for their reliable determination requires large concentrations of  $CH_2Cl_2$ , which could result in change of the physical properties of the medium. The relative fluorescence quantum yields of compounds **I–III** in methylene chloride, as well as the quenching constants of  $CHCl_3$  and  $CCl_4$ , calculated by Eqs. (1) and (2), are given in Table 2.

Positive deviations from the Stern-Volmer equation in the fluorescence quenching of I-III with  $CCl_4$ indicate that the quenching process simultaneously follows two mechanisms, one of which is related to dynamic quenching  $(K_d)$ . The other mechanism  $(K_x)$ involves either static quenching via formation of nonfluorescent complex by the fluorophore and quencher molecule in the ground state or the existence of a quenching sphere that reduces the fraction of fluorescing molecules [14]. The larger fluorescence quenching constant of  $CCl_4$  (Table 2) was attributed to the dynamic constant, taking into account its dependence upon solvent viscosity. The ratio of  $K_{\rm d}$  values for compound I in acetonitrile and 1,4-dioxane is 3.7, which is similar to the viscosity ratio of 1,4-dioxane (1.31 cP [15]) and acetonitrile (0.34 cP [15]), equal to 3.9. By contrast,  $K_x$  does not depend on the viscosity, in keeping with both "nonfluorescent complex" and "quenching sphere" models.

Dynamic quenching is quantitatively characterized by the bimolecular quenching rate constant  $(k_q)$  which is related to the dynamic quenching constant through the equation  $k_q = K_d/\tau_0$ , where  $\tau_0$  is the fluorophore lifetime in the absence of quencher. Insofar as experimental values of  $\tau_0$  for compounds **I–III** are lacking, the effects of particular dipyrrolylbenzene and chloromethane on  $k_q$  can be analyzed only on a qualitative level. The data in Table 2 show that  $k_q$ for the same dipyrrolylbenzene ( $\tau_0$  does not change) increases in the order CH<sub>2</sub>Cl<sub>2</sub> < CHCl<sub>3</sub> < CCl<sub>4</sub>, i.e., in parallel with variation of the electron affinity of these chloromethanes.

Among the examined chloromethanes, carbon tetrachloride quenches fluorescence of dipyrrolylbenzenes **I–III** most effectively. The dynamic quenching constants for compounds **I** and **II** in acetonitrile and compound **II** in *n*-hexane have the maximal values and almost coincide with each other. The values of  $K_d$  for compound **I** in 1,4-dioxane and acetonitrile are proportional to the reciprocal viscosity of these solvents, indicating diffusion-controlled fluorescence quenching of **I** and **II** in CCl<sub>4</sub>. Presumably, the fluorescence quenching rate constant of compound **III** also approaches the diffusion-controlled value, for  $K_d$ decreases only slightly in going from *n*-hexane to acetonitrile, in keeping with the solvent viscosities.  
 Table 2. Fluorescence quenching constants of dipyrrolylbenzenes with chloromethanes in different media and fluorescence quantum yields in methylene chloride

Comp. no.	CCl <sub>4</sub>		CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>		
	$K_{\rm d},$ $1{ m mol}^{-1}$	$K_{x},$ l mol <sup>-1</sup>	$K_{\rm d},$ $1{ m mol}^{-1}$	$\Phi/\Phi_0^{\ a}$		
Ι	40.3	7.0	15.8	0.55		
II	41.6	1.8	5.5	0.77		
III	23.9	3.6	1.7	0.89		
1,4-Dioxane						
Ι	11.0	5.7	7.2	0.63		
<i>n</i> -Hexane						
II	38.0	4.3	4.3	0.89		
III	26.6	1.7	0.25	1.00		
	1					

<sup>a</sup> Fluorescence quantum yields of compounds **I–III** in MeCN, *n*-hexane, and 1,4-dioxane are assumed to be equal to unity.

In the fluorescence quenching with chloroform, the dynamic quenching constant increases in going from di- to monovinyl derivative, and it has the maximal value for unsubstituted dipyrrolylbenzene (Table 2). Insofar as the intrinsic lifetimes of dipirrolylbenzenes are likely to change in the reverse order, even stronger increase of  $k_q$  (as compared to  $K_d$ ) may be expected in the series  $\mathbf{III} < \mathbf{II} < \mathbf{I}$ . Although the dynamic quenching constants for methylene chloride were not determined specially, the fluorescence quantum yields in this solvent (Table 2) show that  $k_q(\mathbf{I}) > k_q(\mathbf{II}) > k_q(\mathbf{II})$ .



**Fig. 4.** Plots of  $I_0/I$  for compound **II** in (1) acetonitrile and (2) *n*-hexane versus concentration of CCl<sub>4</sub>.

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**Table 3.** Fluorescence lifetimes of dipyrrolylbenzenes **I–III**, fluorescence quenching rate constants, and diffusion rate constants of solvents<sup>a</sup>

Comp. no.	$\tau_0 \times \frac{10^9}{s}$ ,	CCl <sub>4</sub>	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	
		$k_{\rm q} \times 10^{-10}, \\ {\rm mol}^{-1},$	$k_{\rm q} \times 10^{-10},$ $\rm mol^{-1}$	$k_{\rm q} \times 10^{-10},$ ${\rm mol}^{-1}$	
MeCN $(k_{dif} 2.0 \times 10^{10}, 1 \text{ mol}^{-1} \text{ s}^{-1})$					
Ι	2.5	1.6	0.63	≤0.003	
II	2.8	1.5	0.20	≤0.001	
III	3.0	0.8	0.06	≤0.0004	
1,4-Dioxane $(k_{dif} 0.5 \times 10^{10}, 1 \text{ mol}^{-1} \text{ s}^{-1})$					
Ι	-	0.44	0.29	≤0.002	
<i>n</i> -Hexane $(k_{dif} 2.3 \times 10^{10}, 1 \text{ mol}^{-1} \text{ s}^{-1})$					
II	-	1.4	0.15	≤0.004	
III	_	0.9	0.08	≤0.0001	

<sup>a</sup> Calculated by the equation  $k_{dif} = 8RT/3000\eta$ , where  $\eta$  is the solvent viscosity.

The lifetimes  $\tau_0$  for compounds **I–III** were estimated using the formulas [16]  $\tau_r = 10^{-4}/\varepsilon_m$  and  $\tau_0 = \Phi_f \tau_r$ , where  $\varepsilon_m$  is the intensity of the most long-wave band in the electronic absorption spectrum, and  $\Phi_f$  is the absolute fluorescence quantum yield of the corresponding dipyrrolylbenzene (Table 1). The values of  $\tau_0$  determined in such a way and  $k_q$  values calculated therefrom are given in Table 3.

It is known that halomethanes, in particular chloromethanes, act as electron acceptors in quenching of electronically excited sites of many aromatic compounds, amines, and some heterocyclic compounds. The electron affinities (EA) of  $CCl_4$ ,  $CHCl_3$ , and CH<sub>2</sub>Cl<sub>2</sub> are 2.12, 1.75, and 1.36 eV, respectively [17]. Dipyrrolylbenzenes I-III are good electron donors. This follows, e.g., from ready electrochemical oxidation of compounds I [5] and III [18]. The ionization potentials (IP) of I-III should be relatively low. In fact, attachment of even one pyrrole ring (IP 8.2 eV) to benzene ring (IP 9.2 eV) gives a conjugated system, 2-phenylpyrrole, whose ionization potential is 7.61 eV [19]. Introduction of one stronger electrondonor pyrrole fragment into the *para* position of the benzene ring should lead to even lower IP values for molecules I-III. Replacement of hydrogen at the nitrogen atom of 2-phenylpyrrole by electron-withdrawing vinyl group increases the ionization potential to 7.76 eV [19]. An analogous effect of vinyl substitution should be observed for compounds I-III. In addition, we calculated the ionization potentials of dipyrrolylbenzenes I-III by the B3LYP/6-311G\* method as the differences between the heats of formation of the corresponding radical cations and neutral molecules in the most favorable conformations. The calculated values are 6.50, 6.62, and 6.78 eV for compounds I, II, and III, respectively. Therefore, they may be ranked as follows according to their ionization potentials: I < II < III.

Taking into account the above considerations, the data in Tables 2 and 3 indicate that the efficiency of fluorescence quenching increases in parallel with the donor power of the substrate and acceptor power of the quencher. Such a relation is typical of reactions following electron transfer mechanism. Our results show that fluorescence quenching of compounds I–III is most likely to involve electron transfer from the molecule of electronically excited dipyrrolylbenzene to chloromethane (in polar solvents) or formation of exciplex (in nonpolar solvents).

Laser photolysis of dipyrrolylbenzenes. Photoexcitation ( $\lambda = 337$  nm) of oxygen-free solutions of compound I in dioxane and of compounds II and III in hexane gives rise to short-lived products whose absorption spectra contain maxima at  $\lambda$  460, 425 and 480, 410, and 530 nm, respectively. Their disappearance follows the first-order kinetics. The kinetic pattern and the rate constant of disappearance of the short-lived products  $(k_T)$  derived from compounds **I**–**III** do not depend on the exciting wavelength. This means that absorbing species of only one type are generated in the above solvents. The lifetimes ( $\tau_T$  =  $1/k_{T}$ ) of the short-lived intermediates in oxygen-free solutions of compound I in 1,4-dioxane and of compounds II and III in *n*-hexane are 23.9, 5.7, and 4.0  $\mu$ s, respectively. In the presence of oxygen, the short-lived products are characterized by considerably shorter lifetimes. Monoexponential kinetics of the decay of photolysis products and shortening of  $\tau_T$ upon saturation of solutions with oxygen allowed us to assign the short-lived products generated by laser photolysis of compounds **I–III** to their triplet states. Low optical densities inherent to T-T transitions must be noted; they indicate low yield of intersystem crossing and are consistent with high absolute fluorescence quantum yields of the compounds under study.

Flash photolysis of solutions of compounds I-IIIin the presence of  $CCl_4$  and  $CHCl_3$  and in  $CH_2Cl_2$  as solvent gives rise to new intermediate species whose disappearance does not follow first-order kinetics and does not depend on the presence or absence of oxygen. The lifetime of triplet states of molecules I-III is not sensitive to the presence of chloromethanes. Fluorescence quenching and the lack of triplet state quenching indicate that the reactive electronically excited state is singlet. The absorption spectra of short-lived intermediates generated by reaction of the singlet



**Fig. 5.** Absorption spectra of the system **III**  $(5 \times 10^{-4} \text{ M})$ -CCl<sub>4</sub> (0.1 M) during flash laser photolysis in (1) acetonitrile and (2) *n*-hexane, recorded in 800 ns after exciting flash.

excited states of **I**–**III** with chloromethanes are shown in Fig. 5 (as an example), and their parameters are collected in Table 4. The spectra were recorded in the presence of oxygen with a view to avoid superposition of T-T absorption.

To elucidate the nature of intermediate products we recorded the electronic absorption spectra of radical cations derived from dipyrrolylbenzenes **I–III**. Radical cations were generated by quenching of the triplet state of a strong electron acceptor, tetrachloro*p*-benzoquinone (**IV**), with compounds **I–III** according to Scheme 3 [20].

As solvent we used acetonitrile. Insofar as compound **IV** and dipyrrolylbenzenes absorb at the wavelength of exciting laser flash ( $\lambda_{ex}$  337.1 nm), the con-

## Scheme 3. $IV + hv \longrightarrow {}^{1}IV,$

 ${}^{1}\mathbf{IV} \longrightarrow {}^{3}\mathbf{IV},$  ${}^{3}\mathbf{IV} + \mathbf{I}(\mathbf{II}, \mathbf{III}) \longrightarrow \mathbf{IV}^{-\cdot} + \mathbf{I}^{+\cdot}(\mathbf{II}^{+\cdot}, \mathbf{III}^{+\cdot}).$ 

centrations of compounds IV and I–III were selected in such a way that more than 90% of light was absorbed by quinone IV. All compounds I–III quench the triplet states of quinone IV. Disappearance of the absorption band corresponding to the triplet state of molecules IV ( $\lambda_{max}$  510 nm [20]) from the NLP spectra is accompanied by appearance of an absorption band belonging to radical anion IV ( $\lambda_{max}$  450 nm [20]), as well as of bands with their maxima at  $\lambda$  500, 490, and 490 nm for compounds I, II, and III, respectively (Fig. 6). The latter were assigned to radical cations of dipyrrolylbenzenes I–III.

The data given in Table 4 show that the absorption



**Fig. 6.** Absorption spectrum of the system **IV**  $(5 \times 10^{-3} \text{ M})$ –**III**  $(5 \times 10^{-5} \text{ M})$  upon flash laser photolysis in acetonitrile, recorded after complete disappearance of the *T*–*T*-absorption.

spectra of the short-lived products generated by reaction of the electronically excited states of compounds **I–III** with chloromethanes are identical to the absorption spectra of the corresponding dipyrrolylbenzene radical cations. An exception was quenching of fluorescence of compound **III** with CHCl<sub>3</sub> and CCl<sub>4</sub> in *n*-hexane. Here, unlike polar acetonitrile, no absorption of **III**<sup>+-</sup> ( $\lambda_{max}$  490 nm) was observed in the NLP spectrum, but a new absorption band appeared with its maximum at ≈410 nm (Fig. 5, Table 4).

Thus, the formation of dipyrrolylbenzene radical cations upon fluorescence quenching of compounds **I–III** with chloromethanes confirms the above conclusion on the quenching mechanism. The formation of solvated radical ions and exciplexes for "classical" fluorescing donor–acceptor systems may be represented by Scheme 4 [21].

**Table 4.** Positions of absorption maxima ( $\lambda$ , nm) of intermediate products formed upon fluorescence quenching of dipyrrolylbenzenes **I–III** with chloromethanes and of the triplet state of tetrachlorobenzoquinone (**IV**) with dipyrrolylbenzenes **I–III** in solvents with different polarities<sup>a</sup>

Comp. no.	CCl <sub>4</sub>	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	IV	
		MeCN	1	1	
Ι	460, <u>500<sup>a</sup></u>	460, 500			
II	480	470, 490	490		
III	470, 490	460, <u>490</u>	490	450, 490	
1,4-Dioxane					
Ι	460, 490	460, 490			
<i>n</i> -Hexane					
Π	460, 480 (sh)	440, 480			
III	_410_	410			

<sup>a</sup> The principal maxima are underscored.

Scheme 4.

$$\begin{array}{c} {}^{1}D^{*} + A \longrightarrow {}^{1}D^{*} \cdots A \xrightarrow{k_{c}} {}^{1}(D^{+}A^{-}) \xrightarrow{k_{d} + k_{fe}} D + A \\ \downarrow \\ {}^{k_{f}} \downarrow \\ D + A \xrightarrow{k_{i}} {}^{(2}D^{+}_{8}\cdots^{2}A^{-}_{8}) \xrightarrow{k_{s}} {}^{2}D^{+}_{s} + {}^{2}A^{-}_{s} \end{array}$$

Here,  ${}^{1}D^{*}$  is an electron donor in the singlet excited state, A is an electron acceptor in the ground state,  ${}^{1}D^{*}\cdots A$  is encounter complex,  ${}^{1}(D^{+} A^{-})^{*}$  is singlet exciplex,  ${}^{2}D_{s}^{+}\cdots 2A_{s}^{-}$  is solvent-separated radical ion pair,  ${}^{2}D_{s}^{+}$  and  ${}^{2}A_{s}^{-}$  are solvated radical ions, and *k* stands for the corresponding rate constants.

In weakly polar solvents ( $\varepsilon < 7$ ) exciplexes cannot dissociate into radical ions [22]. Relatively long-lived radical cations generated in *n*-hexane and 1,4-dioxane (Table 4) exist as salts that are formed as a result of fragmentation of chloromethane radical anion in the exciplex. In keeping with Scheme 2 (D = I, II; A = chloromethane (R–Cl), the process may be represented as follows (D = I):

$$^{1}(\mathbf{I}^{+}\mathbf{R}-\mathbf{Cl}^{-})^{*} \longrightarrow \mathbf{I}^{+}\mathbf{Cl}^{-} + \mathbf{R}$$

The existence of an additional path for deactivation of exciplex is also responsible for the lack of fluorescent properties of exciplexes formed by dipyrrolylbenzenes **I** and **II** with chloromethanes; therefore, they cannot be distinguished spectrally upon fluorescence quenching (Fig. 3). When D = III, fluorescence quenching in *n*-hexane (as well as in MeCN) neither changes the shape of the emission band of the



**Fig. 7.** Change of the electronic absorption spectrum of compound **III** ( $c = 5 \times 10^{-5}$  M) in acetonitrile in the presence of CCl<sub>4</sub> after irradiation ( $\lambda_{exc}$  334 nm) over a period of (1) 0, (2) 5, (3) 10, and (4) 20 s.

monomer nor gives rise to new emission band in the long-wave region, which would indicate formation of a fluorescing exciplex. In this case, radical cation salts  $\mathbf{III}^+$ Cl<sup>-</sup> are not formed, but new species are revealed ( $\lambda_{max}$  410 nm). The latter are formed during the fluorescence lifetime of the monomer. These data indicate high rate of the reaction between the components in the exciplex formed by molecule **III** and CCl<sub>4</sub> or CHCl<sub>3</sub>, which competes with its fluorescence. It should be noted that excitation of **III** in nonpolar CCl<sub>4</sub> gives the same product as that formed upon fluorescence quenching with CCl<sub>4</sub> in hexane. Excitation of **III** in more polar CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> produces radical cation **III**<sup>+</sup>. (Table 4).

Radical cation  $III^+$  is the strongest electrophile among radical cations  $I^+-III^+$ . Presumably, the product formed as a result of photoexcitation of compound III in *n*-hexane in the presence of CCl<sub>4</sub> and CHCl<sub>3</sub> and in pure CCl<sub>4</sub> is neutral radical III –Cl originating from recombination of III<sup>+</sup> and Cl<sup>-</sup> in nonpolar media. Analogous short-lived adducts were proposed as intermediates in the photochemical reaction of biphenyl with CCl<sub>4</sub> [23] and reductive dechlorination of chlorobenzenes in their reactions with electronically excited bichromophoric compounds [24].

The nature of intermediates (are they charged or neutral radicals) is directly reflected in the final products. For all systems where NLP produces detectable radical cations, continuous irradiation of solutions at a wavelength corresponding to absorption of parent dipyrrolylbenzene leads to increase in the absorption intensity at  $\lambda_{max} \approx 600$  nm due to a stable product (Fig. 7). After the photolysis, a blue film and a precipitate (presumably, oligomeric) deposit on the walls and bottom of the cell. If no radical cations are present (only neutral radicals are observed), the solution remains transparent and colorless, and no absorption bands appear in the long-wave region of the spectrum (Fig. 8).

Thus, the presence of chloromethanes gives rise to an additional path of decay of the electronically excited state of dipyrrolylbenzenes I–III, which involves electron transfer from their singlet states to  $CH_2Cl_2$ ,  $CHCl_3$ , or  $CCl_4$  molecule. The triplet states of I–III are inactive in one-electron transfer. Radical cations derived from compounds I–III in nonpolar and moderately polar solvents exist as ion pairs where the positive charge is compensated by negative charge of chloride ion. In nonpolar solvents, such as *n*-hexane and  $CCl_4$ , radical cations of the weakest donor (compound III) combine with  $Cl^-$  to form an adduct like III–Cl.

#### **EXPERIMENTAL**

The IR spectra were recorded in KBr on a Bruker IFS 25 spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Bruker DPX-400 and AV-400 instruments at 400.13 MHz for <sup>1</sup>H and 100.61 MHz for <sup>13</sup>C using HMDS as internal reference. Spectrophotometric measurements were performed on a Perkin-Elmer Lambda 35 spectrophotometer. The fluorescence spectra were measured on a Perkin-Elmer LS 55 luminescence spectrometer. To avoid the effect of photochemical reactions, the scan rate was no lower than 500  $\text{nm}\,\text{min}^{-1}$ . The fluorescence quantum yields were determined relative to anthracene in *n*-hexane  $(\Phi_{f0} 0.3 [16])$  and were calculated with account taken of the refractive indices of the solvents. Nanosecond laser photolysis was performed with the aid of an AIL3 N<sub>2</sub> laser ( $\lambda$  337.1 nm, pulse energy 3 mJ, halfheight pulse duration 7 ns; samples were irradiated in a  $1 \times 1$  cm<sup>2</sup> quartz cell). The experimental setup was described previously [25]. A DRSh-500 mercury lamp was used for stationary photolysis. The excitation wavelength corresponded to the edge of the long-wave absorption band of compound I-III. A quartz cell filled with water (cell path length 5 cm) was used as a heat filter. Solutions were freed from oxygen by purging with argon over a period of 20 min. All solvents (purity 99.9%, Merck) were used without additional purification.

Synthesis of dipyrrolylbenzenes I–III. A solution of 2.00 g of 1,4-diacetylbenzene dioxime in 20 ml of DMSO was added to a mixture of 1.98 g of cesium fluoride and 0.31 g of lithium hydroxide in 10 ml of methanol, and the mixture was stirred for 45 min at 45–50°C. The solvents (methanol and water) were distilled off, the residue (cesium oximate) was transferred into a 0.25-1 rotating steel high-pressure reactor, 50 ml of DMSO was added, and the mixture was saturated with acetylene (initial pressure 14 atm). The mixture was heated to 110°C and was kept for 2 h at that temperature. It was then diluted with water to a volume of 200 ml and extracted with diethyl ether  $(5 \times 15 \text{ ml})$ . The extracts were washed with water  $(3 \times 10 \text{ ml})$  and dried over K<sub>2</sub>CO<sub>3</sub>, and the solvent was distilled off. The residue, 1.67 g, was dissolved in a small amount of diethyl ether, and the undissolved material (compound I) was purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> using DMSO as eluent. Yield 0.34 g (15.7%). The ether solution was separated by column chromatography on Al<sub>2</sub>O<sub>3</sub> (hexane-diethyl ether, 3:1) to isolate 0.16 g (6.6%) of compound II and 0.17 g (6.3%) of III.

**1,4-Bis(1***H***-pyrrol-2-yl)benzene (I).** mp 289–290°C (decomp.); published data [7]: mp 298–307°C.

 $\begin{array}{c} A \\ 0.5 \\ 0.4 \\ 0.3 \\ 0.2 \\ 0.1 \\ 0 \\ 240 \end{array} \begin{array}{c} 1-4 \\ 4-1 \\ 0 \\ 240 \end{array} \begin{array}{c} 4-1 \\ 0 \\ 240 \end{array} \begin{array}{c} 4-1 \\ 0 \\ 240 \end{array} \begin{array}{c} 640 \\ 740 \\ \lambda, \text{ nm} \end{array}$ 

**Fig. 8.** Change of the electronic absorption spectrum of compound **III** ( $c = 5 \times 10^{-5}$  M) in *n*-hexane in the presence of CCl<sub>4</sub> after irradiation ( $\lambda_{exc}$  334 nm) over a period of (1) 0, (2) 5, (3) 10, and (4) 20 s.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 11.23 s (2H, NH), 7.58 s (4H, *o*-H), 6.83 s (2H, 5-H), 6.48 s (2H, 4-H), 6.10 s (2H, 3-H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 131.03, 130.88 (C<sup>2</sup>, C<sup>*i*</sup>), 123.54 (C<sup>*o*</sup>), 119.03 (C<sup>5</sup>), 109.03, 105.14 (C<sup>3</sup>, C<sup>4</sup>). IR spectrum (KBr), v, cm<sup>-1</sup>: 3439, 3389, 3102, 2926, 1665, 1653, 1639, 1601, 1580, 1504, 1461, 1406, 1302, 1242, 1188, 1113, 1035, 1011, 913, 881, 836, 795, 719, 668, 619, 546, 507, 472.

1-(1H-Pyrrol-2-yl)-4-(1-vinyl-1H-pyrrol-2-yl)benzene (II). mp 128–130°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 8.42 s (1H, NH), 7.48 d (2H, *m*-H,  ${}^{3}J = 8.4$  Hz), 7.36 d (2H, *o*-H,  ${}^{3}J = 8.4$  Hz), 7.10 m (1H, 5 $\alpha$ -H), 6.91 d.d (1H, H<sub>X</sub>,  ${}^{3}J_{AX} = 8.8$ ,  ${}^{3}J_{BX} = 15.7$  Hz), 6.87 m (1H, 5-H), 6.55 m (1H, 3-H), 6.30 m (2H, 4-H, 4α-H), 6.26 m (1H, 3α-H), 5.19 d (1H, H<sub>B</sub>,  ${}^{3}J_{BX} = 15.7$  Hz), 4.75 d (1H, H<sub>A</sub>,  ${}^{3}J_{AX} = 8.8$  Hz).  ${}^{13}C$  NMR spectrum (CDCl<sub>3</sub>),  $\delta_{C}$ , ppm: 134.03 ( $C^2$ ), 131.90 ( $C^{\alpha}$ ), 131.66 ( $C^2$ ), 131.61 ( $C^i$ ), 130.18 ( $C^p$ ), 129.69 ( $C^o$ ), 123.68 ( $C^m$ ), 118.99 ( $C^5$ ), 118.47 ( $C^5$ ), 110.17 ( $C^4$ ), 110.03 ( $C^4$ ), 109.98 ( $C^3$ ), 106.27 ( $C^{3'}$ ), 99.02 ( $C^{\beta}$ ). IR spectrum (KBr), v, cm<sup>-1</sup>: 3429, 3365, 1912, 1720, 1606, 1466, 1343. 1318, 1179, 1113, 1074, 1059, 1037, 975, 913, 890, 844, 803, 791, 740, 711, 673, 652, 632, 591, 678, 540, 515, 458, 409. Found, %: C 81.89; H 6.22; N 11.90. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>. Calculated, %: C 82.02; H 6.02; N 11.96.

The spectral parameters and physical constants of 1,4-bis(1-vinyl-1H-pyrrol-2-yl)benzene (III) were reported in [9].

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