The nature of transitions in electronic absorption spectra of radical cations of dipyrroles with phenylene bridging groups

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The electronic absorption spectra of radical cations of dipyrroles with a phenylene bridge were studied by laser flash photolysis and quantum chemical methods. Intense absorption bands of the radical cations in the visible region ($\lambda_{max} \approx 500$ nm, $\varepsilon_{max} > 2 \cdot 10^4$ L mol^{-1} cm^{-1}) are caused by excitation of electrons from single occupied MOs to the LUMO. In the near IR region, calculations predict additional, relatively intense ($f \approx 0.27$—0.29) electronic transitions associated with excitation of electrons from low-lying MOs to the single occupied MO.

Key words: dipyrroles with a phenylene bridge, laser photolysis, radical cations, electronic absorption spectra, quantum chemical calculations, time-dependent density functional theory.

Dipyrroles with phenylene bridging groups (hereinafter reffered to as dipyrrolylbenzenes, DPB) were first synthesized as monomers for the synthesis of low-bandgap polymers and application in optics.[1—4] The spectral-luminescent and photophysical properties of this type of comonomers show high sensitivity to the nature and position of substituents in the pyrrole and benzene rings and the possibility of fine adjustment of their optical properties.[3,5,6] However, the electronic and molecular structures of DPB radical cations, which should to a great extent determine the mechanism of polymerization, as well as the injection and charge-transport properties, are poorly studied. For this reason, investigations of the spectroscopic properties of DPB radical cations are of considerable interest. Information on the electronic spectra of radical cations is also needed for reliable identification and interpretation of the nature of the species formed during the chemical, electrochemical, and photochemical synthesis of polyconjugated systems. The chemical synthesis of the radical cations of pyrrole-containing compounds is strongly complicated by fast polymerization so that the relatively long-lived species can be prepared only if the pyrrole rings have substituents in the α-positions.[7] Consequently, fast generation of radical cations of the DPB having no substituent in the α-positions using nanosecond laser photolysis (NLP) is very efficient when studying their spectral and kinetic properties.

Earlier,[4] we have reported preliminary data on the band positions in the electronic absorption spectra of the radical cations of 1,4-bis(2-pyrrolyl)benzene (**1**), 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)benzene (**2**), and 1,4-bis[2-(1-vinyl-2-pyrrolyl)]benzene (**3**) obtained by the NLP method. In the present work, both experimental studies and quantum chemical calculations of the electronic absorption spectra of the radical cations of compounds **1—3** and of the more recently synthesized 4-(3-methyl-2-pyrrolyl)-1-(2-pyrrolyl)benzene (**4**), 1-(2-pyrrolyl)-4-(1-vinyl-3-methyl-2-pyrrolyl)benzene (**5**), and 4-(1-vinyl-3-methyl-2-pyrrolyl)-1-(1-vinyl-2-pyrrolyl)benzene (**6**) were performed to analyze in more detail the nature of electronic transitions in the spectra of radical cations. As the computational method, the time-dependent density functional theory (TD-DFT) procedure was used.

Experimental

A detailed scheme of the synthesis of DPB **1—3** was described earlier.[4] Compounds **4—6** were prepared by the reaction of 1-acetyl-4-propionylbenzene dioxime with acetylene (Trofimov reaction)[8] (Scheme 1).

The reaction mixture was extracted with diethyl ether. The combined ether extracts were washed with water and dried over K_2CO_3. After removal of the ether, the residue was chromatographed (Al_2O_3, the eluent was hexane—diethyl ether with the gradient from 1 : 0 to 0 : 1). The yields of compounds **4**, **5**, and **6** were 9, 17, and 32%, respectively.

The spectral-kinetic properties of the DPB radical cations were studied on a laser photolysis setup.[9] Excitation of the samples was performed in a quartz cell (1×1 cm^2) using an AIL-3 N_2 laser ($\lambda = 337.1$ nm, pulse energy 3 mJ, the half-amplitude pulse duration 7 ns). The probing source was a DKsSh-120 pulsed xenon lamp (the half-amplitude pulse duration 1 ms). The light from the probing source was passed through a monochromator. A FEU-96 photomultiplier served as the radiation detector. The electronic absorption spectra of the radical cations were obtained pointwise at 10 nm intervals immediately after the DPB

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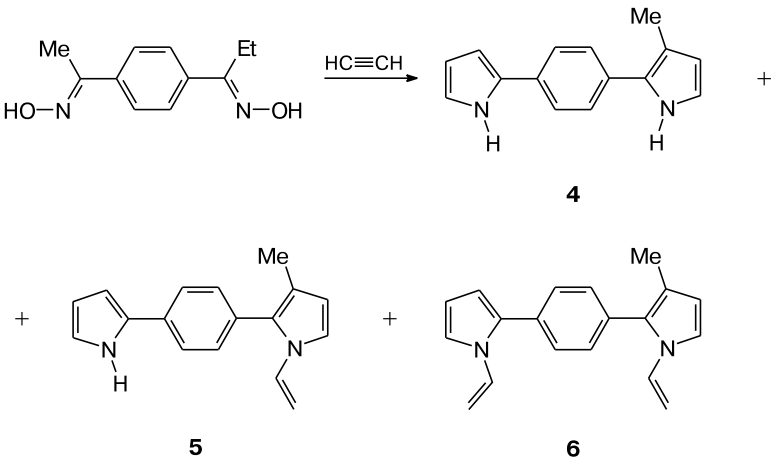
Scheme 1



fluorescence decay. Oscillograms were recorded on a Tektronix TDS 2022 oscillograph.

The solvent, acetonitrile (99.9%, Merck), was used as is. Oxygen was removed from solutions by blowing argon for 20 min.

Quantum chemical calculations were carried out using the GAUSSIAN 03W program package.[10] Geometry optimization of the parent DPB molecules and their radical cations was performed within the framework of the density functional theory (DFT) using the B3LYP exchange-correlation functional. The TD-DFT method was applied for calculations of the electronic transition energies of the radical cations.[11,12]

Results and Discussion

Analysis of the literature data on the radical cations of the pyrrole systems showed that the spectra of the radical cations in the visible and near UV region exhibit two absorption bands. For example, 2,2′-bipyrrole (obtained by pulse radiolysis) is charaterized by the bands at $\lambda_{max} = 360$ nm ($\varepsilon = 27000$ L mol^{-1} cm^{-1}) and $\lambda_{max} = 580$ nm ($\varepsilon = 6200$ L mol^{-1} cm^{-1}).[13] The spectrum of the radical cations of 5,5′-diphenyl-2,2′-bipyrrole (chemical generation) shows the absorption bands at $\lambda_{max} = 486$ and 780 nm,[14] the second band being ~1.5-fold less intense than the first one. The shorter-wavelength and more intense absorption bands are assigned[13,14] to the transitions caused by electron excitation from the single occupied molecular orbital (SOMO) to the unoccupied MOs and the long-wavelength and less intense bands are assigned to the transitions caused by electron excitation from the deep-lying occupied MOs to the SOMO. The examples given above illustrate the influence of the conjugation chain length on positions of two transitions in the spectra of the radical cations. Both transitions undergo a bathochromic shift as the size of the π-system increases.

The electronic absorption spectra of the DPB radical cations were recorded in the wavelength region 360—650 nm where they appear as single bands with maxima near $\lambda \approx 500$ nm (Fig. 1, Table 1). These spectra can be assigned to the transitions caused by electron excitation from the deep-lying MOs to the SOMO or to the transitions from the SOMO to the unoccupied orbitals. The

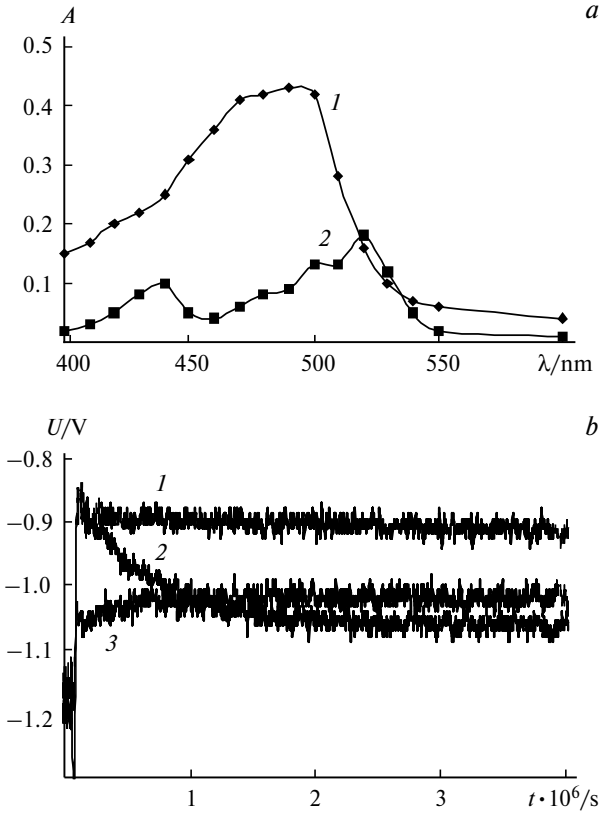


Fig. 1. Laser photolysis of the system **5** + PTZ in MeCN—$CHCl_3$ (10 vol.%): absorption spectra obtained immediately after excitation (*1*, $\mathbf{5}^{+\bullet}$) and after 3 μs (*2*, $PTZ^{+\bullet}$) (*a*); kinetic curves obtained in the absence of PTZ at $\lambda = 490$ nm (*1*) and in the presence of PTZ at $\lambda = 490$ (*2*) and 520 nm (*3*) (*b*); PTZ is phenothiazine.

Table 1. Spectral characteristics of the radical cations of DPB in MeCN

Radical cation	λ_{max}/nm	ε_{max}/L mol^{-1} cm^{-1}
1	500	28000
2	480	25000
3	490	23000
4	500	26000
5	490	24500
6	490	22000

effect of the conjugation chain length on positions of the absorption bands of the radical cations of the pyrrole systems (see above) enables a tentative assignment of the observed transition to the shortwave transitions in the spectra of the radical cations of 2,2′-bipyrrole and 5,5′-diphenyl-2,2′-bipyrrole.

For more reliable assignment and comparison with the results of calculations, the molar absorptivities of the DPB radical cations were determined in the present work by the method of cascade electron transfer according to Scheme 2.

Scheme 2

$$DPB + h\nu_a \xrightarrow{i} {}^1DPB^* \quad (1)$$

$${}^1DPB^* \xrightarrow{ii} DPB \quad (2)$$

$${}^1DPB^* \xrightarrow{iii} DPB + h\nu_f \quad (3)$$

$${}^1DPB^* \xrightarrow{iv} {}^3DPB \quad (4)$$

$${}^1DPB^* + CH_3Cl \xrightarrow{v} DPB^{+\cdot} + {}^{\cdot}CH_3 + Cl^- \quad (5)$$

$$DPB^{+\cdot} + PTZ \xrightarrow{v} DPB + PTZ^{+\cdot} \quad (6)$$

$$DPB^{+\cdot} \xrightarrow{vi} P \quad (7)$$

P are products.

i is light absorption; *ii* is internal conversion; *iii* is fluorescence; *iv* is intersystem crossing; *v* is electron transfer; *vi* is formation of products.

DPB radical cations were reduced with PTZ, which has one of the lowest first ionization potentials among organic compounds; this *a priori* ensures thermodynamically favourable conditions for the electron-transfer reaction (6). Furthermore, the $PTZ^{+\cdot}$ radical cation has a typical and well studied electronic absorption spectrum,[15,16] which facilitates the assignment of the intermediates of reaction (6). The PTZ concentration was chosen in such a manner that all $DPB^{+\cdot}$ be consumed in reaction (6) (see Scheme 2). In this case, the following equality holds for the concentrations

$$[DPB^{+\bullet}]_{t=0} = [PTZ^{+\bullet}]_{t=\infty}$$

and the molar absorptivities of the $DPB^{+\cdot}$ radical cations can be calculated using the equation

$$\varepsilon_{max}(DPB^{+\bullet}) = \varepsilon_{520}(PTZ^{+\bullet})A_{max}(DPB^{+\bullet})/A_{520}(PTZ^{+\bullet}),$$

where $A_{max}(DPB^{+\cdot})$ is the optical density at λ_{max} of the corresponding DPB at the $t = 0$, $A_{520}(PTZ^{+\cdot})$ is the optical density of $PTZ^{+\cdot}$ measured after the complete disappearance of $DPB^{+\cdot}$.

The molar absorptivity of $PTZ^{+\cdot}$ was taken equal to 9300 L mol^{-1} cm^{-1} at $\lambda_{max}(PTZ^{+\cdot}) = 520$ nm.[16] An example of cascade electron transfer is given in Fig. 1. The experimental data are listed in Table 1. The resulting high band intensities with $\varepsilon_{max} > 2 \cdot 10^4$ L mol^{-1} cm^{-1} (see Table 1) enable a more reliable confirmation of the assignment made above.

To specify the nature of the absorption bands in the spectra of the radical cations, the electronic transition energies were calculated within the framework of time-dependent density functional theory. The geometry of the radical cations in the doublet ground state was optimized using the UB3LYP method in the 6-31+G(d) basis set. In all calculations, the error of the spin-unrestricted method due to the admixing of higher multiplicity spin states (spin contamination) was negligible (for all radical cations, the squared total spin values were $\langle S^2 \rangle \leq 0.77$ and differed by less than 3% from the expected theoretical value $s(s + 1) = 0.75$). Analysis of the bond length along the skeleton of the parent DPB molecules and of their radical cations (Fig. 2) shows that ionisation causes the molecules to undergo significant structural rearrangement toward the formation of quinonoid structures. Namely, the longitudinal bonds in the molecules are shortened, while the adjacent cross bonds are elongated (see Fig. 2). As a consequence, the dihedral angles between the central benzene ring and the peripheral pyrrole rings decrease.

The transition energies and oscillator strengths in the gas phase were calculated using the TD-UB3LYP method in the 6-31+G(d) basis set. As shown elsewhere, the introduction of a single diffusion function considerably increases the accuracy of calculations of the transition energy by the TD-DFT method, whereas the introduction of one more diffusion function (++) increases the quality of calculations to a much lesser extent.[17]

The energies and oscillator strengths of the first eight electronic transitions were calculated for each molecule. The theoretical spectra of the radical cations of compounds **1—5** exhibit only two (radical cations of DPB **1—4**) or three (radical cation of DPB **5**) intense $\pi\pi^*$-transitions in the wavelength region 300—850 nm (Table 2). The more intense ($f > 0.7$) shortwavelength transitions $D_6 \leftarrow D_0$

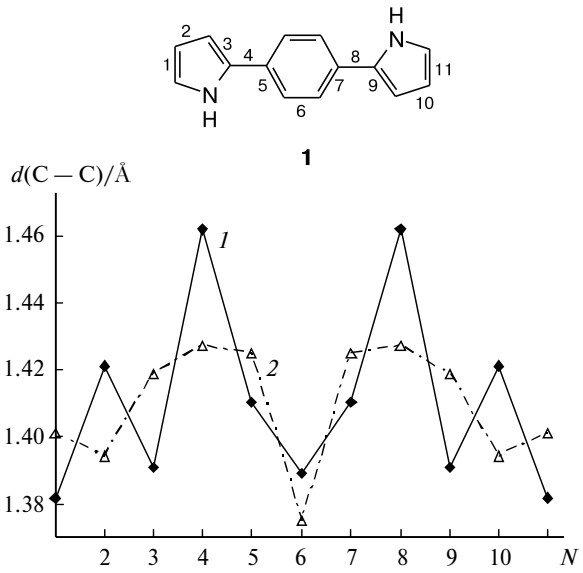


Fig. 2. Atomic numbering scheme, atomic numbers (*N*) and optimized bond lengths (*d*) in neutral molecule **1** (obtained from RB3LYP/6-31+G (d) calculations) (*1*) and in the radical cation of **1** (obtained from UB3LYP/6-31+G(d) calculations) (*2*).

($D_5 \leftarrow D_0$ for **1** and **4**) at λ ~410 nm were correlated with the high-intensity transitions ($\varepsilon > 2 \cdot 10^4$ L mol^{-1} cm^{-1}) observed in the experimental spectra of the $DPB^{+\cdot}$ radical cations at λ_{max} ~500 nm (see Fig. 1, Table 1). According to calculations, the major contribution to these transitions comes from the configuration SOMO → LUMO (LUMO is the lowest unoccupied MO). The less intense long-wavelength transitions $D_1 \leftarrow D_0$ ($f \approx 0.27$—0.29) with the major contributions from the configuration SOMO-1 → SOMO (radical cations of DPB **1**—**4**) and two transitions, $D_1 \leftarrow D_0$ and $D_2 \leftarrow D_0$, in the case of the radical cation of compound **5**, are caused by mixing of the electron excitations SOMO-1 → SOMO and SOMO-2 → SOMO. They lie in the region λ > 800 nm. The MOs involved in the transitions discussed (shown for the radical cation of compound **4** as an example) and the designations of the transitions in accordance with Ref. 18 are given in Fig. 3. Unfortunately, the A-type transitions lie beyond the spectral range of the NLP setup used and could not be observed in the experimental spectra. To elucidate whether the TD-DFT method can correctly predict the A-type transitions for the radical cations of DPB-like tricyclic conjugated systems, we additionally calculated the radical cation of *p*-terphenyl (**7**) whose experimental spectrum is known up to the near-IR region. According to published data, two absorption bands of the radical cation of **7** at λ_{max} = 460 and 965 nm are due to the B-type and A-type transitions, respectively.[19] As seen from Table 2, the calculated values

Table 2. Calculated energies and oscillator strengths of vertical electronic transitions in the radical cations of DPB[a] in the gas phase

Radical cations	Configuration	Transition	λ/nm	*f*
1	**0.86A_1**	**$D_1 \leftarrow D_0$**	**801.34**	**0.2806**
		$D_2 \leftarrow D_0$	579.99	0.0000
		$D_3 \leftarrow D_0$	564.19	0.0106
		$D_4 \leftarrow D_0$	509.63	0.0000
	0.87B_1	**$D_5 \leftarrow D_0$**	**409.65**	**0.8825**
		$D_6 \leftarrow D_0$	386.92	0.0000
		$D_7 \leftarrow D_0$	355.77	0.0000
		$D_8 \leftarrow D_0$	318.50	0.0058
2	**0.85A_1**	**$D_1 \leftarrow D_0$**	**832.53**	**0.2784**
		$D_2 \leftarrow D_0$	763.12	0.0236
		$D_3 \leftarrow D_0$	578.31	0.0048
		$D_4 \leftarrow D_0$	528.00	0.0007
		$D_5 \leftarrow D_0$	419.53	0.0793
	0.84B_1	**$D_6 \leftarrow D_0$**	**410.82**	**0.7120**
		$D_7 \leftarrow D_0$	375.43	0.0094
		$D_8 \leftarrow D_0$	358.80	0.0026
3	**0.85A_1**	**$D_1 \leftarrow D_0$**	**861.13**	**0.2962**
		$D_2 \leftarrow D_0$	774.4	0.0003
		$D_3 \leftarrow D_0$	773.36	0.0288
		$D_4 \leftarrow D_0$	554.35	0.0000
		$D_5 \leftarrow D_0$	436.37	0.0000
	0.89B_1	**$D_6 \leftarrow D_0$**	**412.61**	**0.7052**
		$D_7 \leftarrow D_0$	400.02	0.0285
		$D_8 \leftarrow D_0$	372.49	0.0000
4	**0.86A_1**	**$D_1 \leftarrow D_0$**	**817.57**	**0.2776**
		$D_2 \leftarrow D_0$	625.92	0.0113
		$D_3 \leftarrow D_0$	570.13	0.0061
		$D_4 \leftarrow D_0$	512.19	0.0002
	0.88B_1	**$D_5 \leftarrow D_0$**	**409.89**	**0.8416**
		$D_6 \leftarrow D_0$	387.78	0.0049
		$D_7 \leftarrow D_0$	357.92	0.0030
		$D_8 \leftarrow D_0$	319.94	0.0052
5	**0.69A_1 + 0.64A_2**	**$D_1 \leftarrow D_0$**	**911.74**	**0.1246**
	−0.52A_1 + 0.77A_2	**$D_2 \leftarrow D_0$**	**822.29**	**0.1798**
		$D_3 \leftarrow D_0$	580.77	0.0054
		$D_4 \leftarrow D_0$	531.52	0.0030
		$D_5 \leftarrow D_0$	426.82	0.0136
	0.86B_1	**$D_6 \leftarrow D_0$**	**411.53**	**0.6256**
		$D_7 \leftarrow D_0$	381.56	0.0988
		$D_8 \leftarrow D_0$	367.10	0.0007
7		$D_1 \leftarrow D_0$	944.16	0.0001
		$D_2 \leftarrow D_0$	930.71	0.0005
	0.88A_1	**$D_3 \leftarrow D_0$**	**805.04**	**0.3867**
		$D_4 \leftarrow D_0$	756.59	0.0000
		$D_5 \leftarrow D_0$	489.43	0.0000
	0.90B_1	**$D_6 \leftarrow D_0$**	**385.30**	**0.6533**
		$D_7 \leftarrow D_0$	371.48	0.0540
		$D_8 \leftarrow D_0$	342.55	0.0000

[a] Transitions with $f > 0.1$ are given in bold.

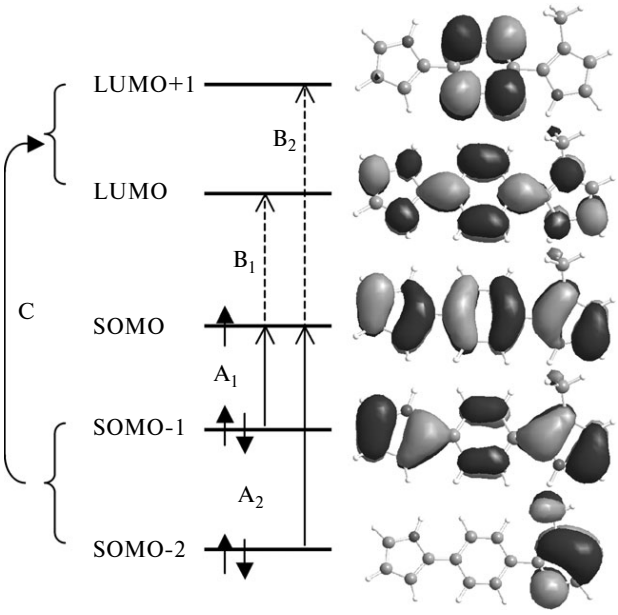


Fig. 3. Notations of transitions[18] and the MOs of the radical cation of **4** obtained by the UB3LYP/ 6-31G+(d) method.

365.3 nm for the B-type transition and 805.04 nm for the A-type transition differ from the corresponding experimental values by 0.55 and 0.25 eV, respectively. Agreement with the experimental data should be considered satisfactory, especially given that the calculations were performed for the gas phase while the experimental data were obtained in solution.

Summing up, our experimental and theoretical study of the electronic absorption spectra of the radical cations of compounds **1**—**6** showed that the absorption bands of the DPB radical cation observed in the visible region at $\lambda_{max} \approx 500$ nm are caused by the B-type transitions. In the near-IR region, TD-DFT calculations predict one (radical cations of DPB **1**—**4**) or two (the radical cation of compound **5** and, possibly, **6**) relatively intense A-type transitions at λ ~800—900 nm.

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