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Effect of pressure on intersystem transitions in aromatic amine molecules

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Luminescence spectra of carbazole, diphenylamine, tri-*p*-tolylamine and N,N′-diphenyl-N,N′-bis(3-methylphenyl)-(1,1′-diphenyl)-4,4′-diamine solutions in toluene and various polymer matrices have been studied at 5 and 295 K. The probability of intersystem crossing from the first singlet excited state S_1 to the triplet one T_1 has been found to depend on the molecule chemical nature, its spatial structure, and interaction with the environment and to increases as the polymer matrix density rises, under applied external uniaxial pressure as well as under influence of external heavy bromine atom.

Исследованы спектры люминесценции растворов карбазола, дифениламина, три-*p*-толиламина и N,N'-дифенил-N,N'-бис(3-метилфенил)-(1,1′-дифенил)-4,4′-диамина в толуоле и различных полимерных матрицах при 5 и 295 К. Установлено, что вероятность интеркомбинационной конверсии из первого синглетного возбужденного S_1 в триплетное состояние T_1 зависит от химической природы молекулы, ее пространственного строения и взаимодействия с окружением и возрастает при увеличении плотности полимерной матрицы, при приложении внешнего одноосного давления, а также под влиянием внешнего тяжелого атома брома.

Polystyrene (PS) and polycarbonate (PC) films containing aromatic amines in high concentrations (about 1 M) or amorphous films formed by aromatic amine deposition are used as hole transporting layers in electro-photography receivers for xerox devices and laser printers [1] or in luminescent diodes [2]. The functions of transporting and emitting layers in an electroluminescence diode can be combined by introducing molecular fragments of phenyl- substituted amines into a polymer macromolecule [3]. In practice, tri-*p*-tolylamine (TTA) and N,N′-diphenyl-N,N′-bis(3-methylphenyl)-(1,1′-diphenyl)-4,4′-diamine (TPD) molecules are used most often.

In the course of electro-photographic process, the photoreceiver surface is charged in air using a corona discharge that is accompanied by UV emission, formation of singlet oxygen, ozone and nitrogen oxides [1, 4]. As a result, various photochemical reactions run in the photoreceiver, in particular, photocyclization of phenyl-substituted amines into carbazoles. This reaction occurs as a rule under the molecule excitation into the lowest triplet state T_1 [5, 6]. Besides, the non-radiative S_1–T_1 transition from the first singlet excited state (S_1) to T_1 one (intersystem crossing) is of great importance in deactivation of electron-excited molecules [7, 8]. Although the S_1–T_1 transition as well as radiative (phosphorescence) and non-radiative (intersystem degradation of the electron energy) transitions from the T_1 state to the ground S_0

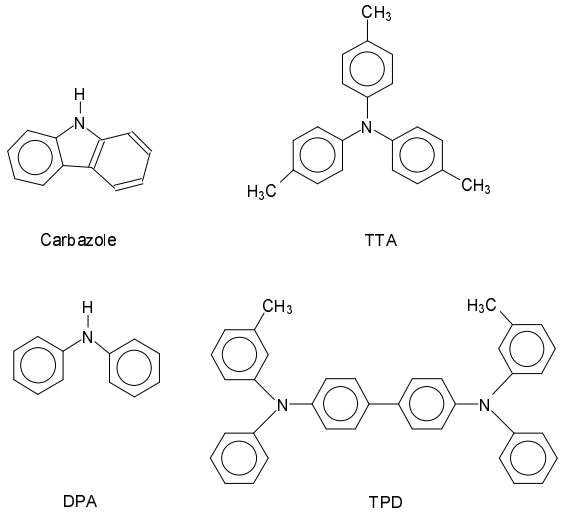

Fig. 1. Structure formulas of carbazole, DPA, TTA and TPD.

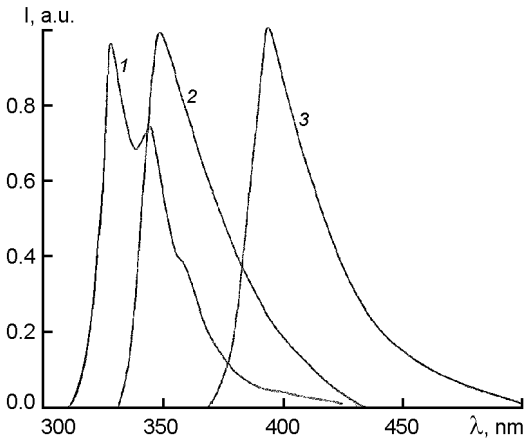

Fig. 2. Fluorescence spectra ($\lambda_{ex.}$ = 313 nm, T = 295 K) of carbazole (*1*), DPA (*2*) and TPD (*3*) in toluene ($C = 10^{-5}$ M).

one are spin-forbidden, the prohibition is eliminated in part due to the spin-orbit interaction that mixes the singlet and triplet molecular states. The probability of the transitions mentioned depends both on features of the molecule itself and on its interaction with the environment [7, 9, 10]. During the xerox or laser printer operation as well as in flexible electroluminescent screens, the polymer layers are subjected to mechanical loading. Therefore, it is of interest to study the effect of uniaxial pressure on the probability of intersystem transitions in aromatic amine molecules.

In this work, the fluorescence (Fl) and phosphorescence (Ph) spectra are studied and the Fl quantum yield values (Φ_{Fl}) and Ph decay time (τ_{Ph}) values are determined for carbazole, diphenylamine (DPA), TTA, and TPD molecules in toluene. To establish a dependence of the S_1–T_1 and T_1–S_0 intersystem crossings probability on the polymer matrix density (ρ), Fl and Ph spectra of TTA and TPD molecules in polyethylene (PE), polystyrene (PS), poly-(4-bromo)styrene (4BrPS), polycarbonate (PC) and polyvinyl chloride (PVCl) are studied as well as Fl and Ph spectra of TTA and TPD in PS, 4BrPS and PC under applied uniaxial pressure (3 kbar). The structure formulas of the studied molecules are presented in Fig. 1.

The polymer and aromatic amines preparations were dissolved in toluene. The 10 to 100 μm thick films were obtained by pouring the solutions onto metal substrates and drying at room temperature. The Fl and Ph spectra were recorded using a SDL-1 spectrometer and a high-pressure mercury lamp with a set of absorbing glass light filters as the excitation source. For low-temperature experiments, an optical helium cryostat was used with molten quartz windows provided with automatic temperature stabilization system. The absolute Fl quantum yields for TTA and TPD were determined in relation to the Fl yield of triphenylamine solution in toluene that gives $\Phi_{Fl} \approx 0.045$ at 295 K [8]. To measure τ_{Ph}, the continuous exciting emission of the mercury lamp was chopped by a mechanical shutter and the section of Ph spectrum isolated by a monochromator (the spectral slot width was less than 0.4 nm) was recorded using a PMT. The signals were processed by a PC.

To provide a high pressure, a special micro-clamp was used consisting of two 2 mm thick steel plates that were drawn together using two screws. The upper plate was provided with a 8 mm dia. orifice closed by a 6 mm thick sapphire window. The sample was placed between the lower plate and the sapphire window. The microclamp with the sample and temperature sensor and heater connected thereto was fixed on a manipulator and placed into the working chamber of the cryostat. During the measurements, the sample was surrounded with helium vapor. The absolute pressure applied to the sample was determined at room temperature from the shift of ruby crystal luminescence line R_1 = 14405 cm^{-1} that shows a bathochromic shift by 0.753 cm^{-1}/kbar as the pressure increases within 0–300 kbar range [11].

Now let the connection be considered between the chemical structure of an amine molecule and its luminescence properties in liquid and frozen toluene solution ($\lambda_{ex.}$ = 313 nm,

$C = 10^{-5}$ M). In Fig. 2, presented are the Fl spectra (T = 295 K) of carbazole, DPA and TPD. The carbazole solution spectrum is seen to be of distinctly vibrational structure (curve *1*). In contrast, the spectra of DPA solution (curve *2*) as well as of TTA and TPD (curve *3*) ones consist of a broad structureless band. The maximum positions of the initial Fl spectra (λ_{max}^{Fl}) as well as Φ_{Fl} values for carbazole, DPA, TTA and TPD are presented in the Table below. Note that the Fl spectra of carbazole and DPA solutions in toluene (T = 295 K) are identical in shape to spectra of solutions in ethanol and cyclohexane [12, 13].

The luminescence spectra of frozen (T = 5 K) toluene solutions of carbazole, DPA, TTA and TPD are presented in Fig. 3. The structural Ph is observed in all the frozen solutions, while no vibrational structure appears in the spectra of frozen DPA and TTA solutions. The absence of said structure in the Fl spectra of liquid DPA, TTA and TPD solutions as well as in those of frozen DPA and TTA solutions appears to be due to inhomogeneous expansion caused by non-rigid molecular structures. This is evidenced by the distinct vibrational structure in the Fl spectrum of carbazole solution (T = 295 K) and the absence of that structure in the DPA spectrum (Fig. 2), the molecules of those compounds contain 8 each but have the rigid planar structure and non-rigid non-planar one, respectively [10]. The Table characterizes the positions of λ_{max}^{Fl}, maximum positions of the initial Ph spectra (λ_{max}^{Ph}), the energy intervals between the Fl band maximum and the initial band of Ph spectrum ($E_{max}^{Fl} - E_{max}^{Ph}$), the ratios of Ph and Fl quantum yields (Φ_{Ph}/Φ_{Fl}) and τ_{Ph} values for carbazole, DPA, TTA and TPD solutions in toluene (T = 5 K). It has been established that, when passing from toluene solutions to PS matrix, the Φ_{Fl} (T = 295 K) for said molecules remain constant to within 10 %, while as the temperature is lowered down to 5 K, the Φ_{Fl} values for the molecules in PS become 15 to 20 % higher.

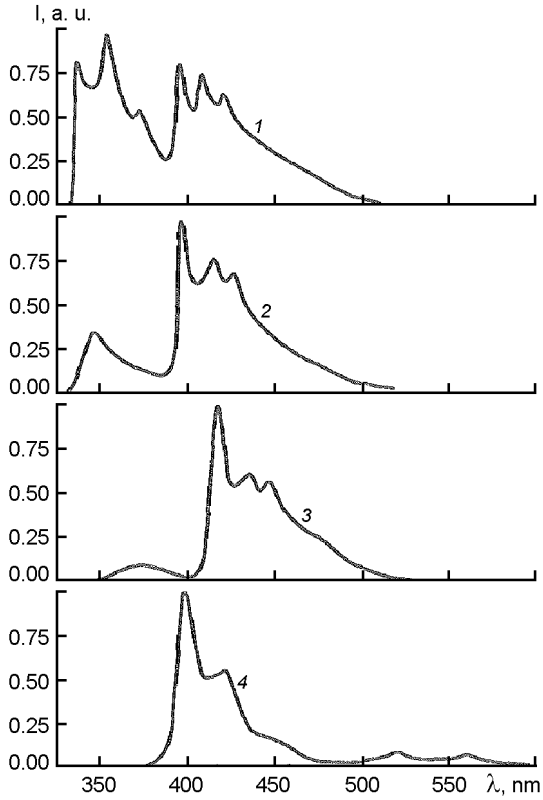

Fig. 3. Fluorescence and phosphorescence spectra ($\lambda_{ex.}$ = 313 nm, T = 5 K) of carbazole (*1*), DPA (*2*), TTA (*3*) and TPD (*4*) in toluene ($C = 10^{-5}$ M).

It follows from the Table that in the DPA-TTA-TPD sequence, that is, as the molecular π-system size enlarges, the λ_{max}^{Fl} and λ_{max}^{Ph} positions show a smooth bathochromic shift and the $E_{max}^{Fl} - E_{max}^{Ph}$ interval diminishes, like to the situation observed for linear polyacenes [10]. Moreover, DPA and TTA molecules show a very low Fl quantum yield. It has been shown [8] that at low temperatures, it is just the intersystem crossing that is the main mechanism of non-radiative deactivation of the S_1 state of complex aromatic molecules, including

Table. Luminescence parameters of carbazole, DPA, TTA and TPD in toluene

Molecule	T = 295 K		T = 5 K				
	λ_{max}^{Fl}, nm	Φ_{FL}	λ_{max}^{Fl}, nm	λ_{max}^{Ph}, nm	$E_{max}^{Fl} - E_{max}^{Ph}$, eV	Φ_{Ph}/Φ_{Fl}	τ_{Ph}, s
Carbazole	340	0.38	335	395	0.56	1	5
DPA	350	0.08	345	398	0.48	3	2
TTA	370	0.05	370	417	0.38	7	0.8
TPD	395	0.27	400	520	0.72	0.1	1.3

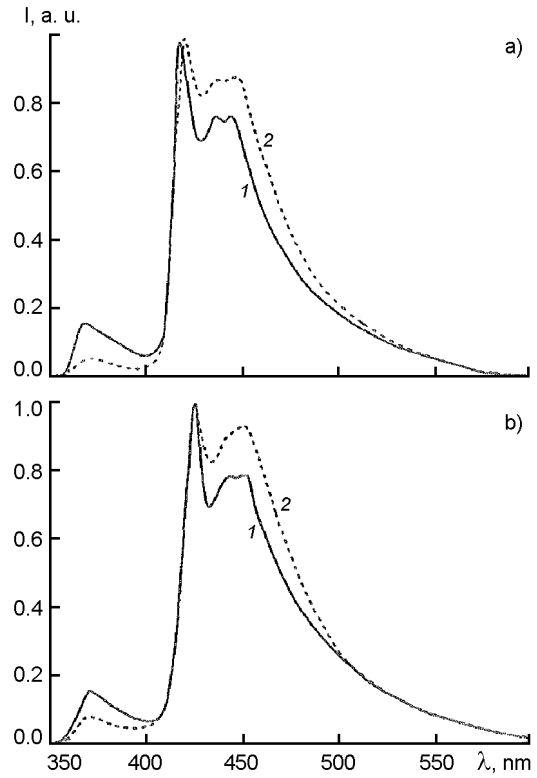

Fig. 4. Fluorescence and phosphorescence spectra ($\lambda_{ex.}$ = 313 nm, T = 5 K) of TTA ($C = 10^{-5}$ M): a) in PE (*1*) and PVCl (*2*); b) in PS (*1*) and 4BrPS (*2*).

DPA, the quantum yield of said process in the latter compound being close to unity. It is known [7, 9] that the S_1–T_1 and T_1–S_0 transition probabilities in a molecule depend on the spin-orbit interaction strength and the energy difference of the states being mixed. Unlike the carbazole molecule, the $2p_Z$ orbital of lone electron pair of the nitrogen heteroatom in DPA and TTA is oriented (due to spatial structure of the molecules) not parallel to $2p_\pi$ orbitals of phenyl ring but at a certain angle thereto. Therefore, the probability of S_1–T_1 and T_1–S_0 intersystem transitions in such molecules must be higher than in carbazole [10]. It is seen from the Table that, when passing from carbazole to DPA having a similar value of $E_{max}{}^{Fl} - E_{max}{}^{Ph}$ interval, the Φ_{Fl} and τ_{Ph} values decrease while the Φ_{Ph}/Φ_{Fl} ratio increases. Thus, the changes in above-mentioned characteristics associated with passing from carbazole to DPA and TTA are due mainly to increase of the spin-orbit interaction caused by the molecular structure non-planarity. When passing from DPA and TTA to TPD, the Φ_{Ph}/Φ_{Fl} ratio decreases while the Φ_{Fl} and τ_{Ph} values increase. Therefore, it can be supposed that the higher Φ_{Fl} value for TPD is due mainly to lowered probability of the S_1–T_1 intersystem crossing caused by increased energy difference between S_1 and T_1 levels.

Now let the luminescence spectra be considered for the aromatic amines in polymer matrices. In Fig. 4, presented are the Fl and Ph spectra ($\lambda_{ex.}$ = 313 nm, T = 5 K) of TTA ($C = 10^{-5}$ M) in PE, PVCl, PS and 4BrPS matrices and in Fig. 5, similar spectra for TPD ($C = 10^{-5}$ M) in PS, PC, and 4BrPS. It is seen that, when passing from frozen toluene solutions to those in polymer matrices, the vibrational structure of TTA and TPD molecular spectra becomes smeared, as well as that the relative Ph intensity (that is, the Φ_{Ph}/Φ_{Fl}) increases. The changes in spectra intensify in the above-mentioned sequences of polymers. For example, the Φ_{Ph}/Φ_{Fl} ratio becomes approximately doubled when passing from PE to PVCl for TTA or from PS to PC for TPD. The mentioned changes in TTA and TPD spectra are

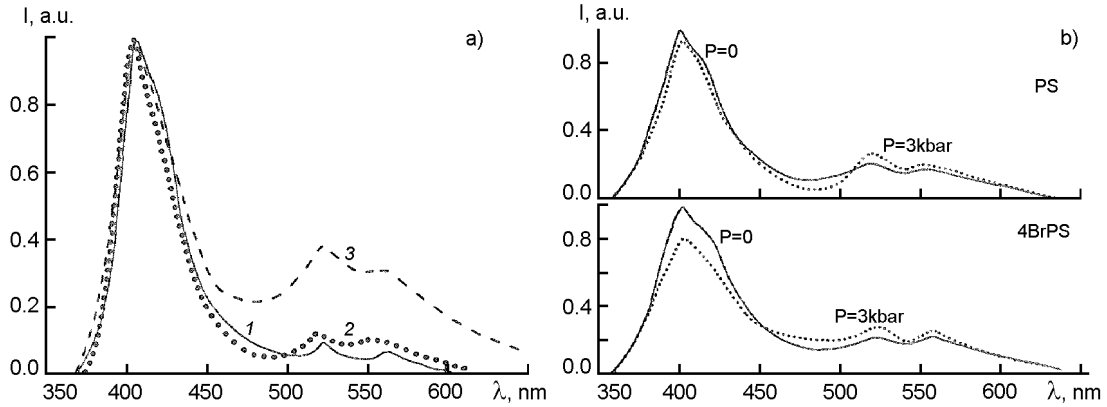

Fig. 5. Fluorescence and phosphorescence spectra ($\lambda_{ex.}$ = 313 nm, T = 5 K) of TPD ($C = 10^{-5}$ M): a) in PS (*1*), PC (*2*) and 4BrPS (*3*); b) in PS and 4BrPS under pressure P = 0 and 3 kbar.

in correlation with increasing density (ρ) of the polymer matrix ($\rho \approx 0.92$; 1.05; 1.2 and 1.4 g/cm^3 for PE, PS, PC and PVCl, respectively). However, τ_{Ph} is not changed appreciably when passing from the frozen toluene solution to solutions in said polymers. At the same time, when PS matrix is changed to 4BrPS, Φ_{Fl} and τ_{Ph} values become approximately halved for all the molecules studied, while the Φ_{Ph}/Φ_{Fl} ratio increases twice or thrice (see, e.g., Figs. 5a and 5b).

In Fig. 5b, presented are the Fl and Ph spectra ($\lambda_{ex.} = 313$ nm, $T = 5$ K) of TPD ($C = 10^{-3}$ M) in PS and 4BrPS matrices measured prior to and after application of uniaxial pressure (3 kbar). The spectral positions of Fl and Ph bands is seen to be not influences by the pressure while the Ph intensity increases. These changes are more pronounced when 4BrPS matrix is substituted for PS one. It has been established also that the τ_{Ph} of TPD remains unchanged under the pressure. Similar results have been obtained for TTA in PS, PC and 4BrPS matrices. The changes in luminescence properties of the amines due to the PS matrix substitution by 4BrPS are explained by the strengthening of spin-orbit interaction in the molecule caused by the external heavy bromine atom [7, 9]. The Φ_{Ph}/Φ_{Fl} increase accompanied by decreased Φ_{Fl} and shortened τ_{Ph} evidence a higher probability of S_1–T_1 and T_1–S_0 intersystem crossings due to mixing of electron wave functions of the amine molecule and the bromine atom. At the same time, the changes in TTA and TPD spectra due to increasing matrix density attained by the replacement of the latter or by the pressure application (when Φ_{Ph}/Φ_{Fl} increases but τ_{Ph} remains unchanged) show that only the S_1–T_1 intersystem crossing probability increases as the matrix ρ rises, while the probabilities of both radiative and non-radiative T_1–S_0 intersystem crossing probabilities are not changed appreciably. The increase of the S_1–T_1 intersystem crossing probability may be due to to (1) intensified mixing of electron wave functions of the amine molecule and the polymer matrix at shortened molecular interdistances that is especially pronounced as PS is replaced by 4BrPS (Fig. 5b) or (2) changes in the molecular spatial structure evidenced by smeared vibrational structure in luminescence spectra arising when toluene is replaced by a polymer matrix (Fig. 2 and 5b).

Thus, it has been shown that the lowered fluorescence quantum yield of DPA and TTA as compared to TPD is associated with the smaller energy difference between S_1 and T_1 levels in the former molecules. At the same time, the lowered fluorescence quantum yield of DPA, TTA and TPD as compared to carbazole is due mainly to the non-planar structure thereof that resulta in strengthened spin-orbit interaction. It has been shown also that the probabilities of S_1–T_1 and T_1–S_0 intersystem crossings in the studied amine molecules depend heavily on the interaction with the environment and increase under influence of the external bromine atom. Moreover, the S_1–T_1 intersystem crossing probability in TTA and YPD molecules increases as the polymer matrix density increases (attained by its replacement or under the external pressure); this may be due to intensified mixing of electron wave functions of the amine molecule and the polymer matrix at shortened molecular interdistances as well as to changes in the molecular spatial structure of the amine.

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Вплив тиску на інтеркомбінаційні переходи молекул ароматичних амінів

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Досліджено спектри люмінесценції розчинів карбазолу, дифеніламіну, три-*n*-толіламіну і N,N′-дифеніл-N,N′-біс(3-метилфеніл)-(1,1′-діфеніл)-4,4′-діаміна у толуолі та різноманітних полімерних матрицях при 5 та 295 К. Встановлено, що імовірність інтеркомбінаційної конверсії з першого синглетного збудженого стану S_1 у триплетний стан T_1 залежить від хімічної природи молекули, її просторової конфігурації та взаємодії з оточенням і збільшується із збільшенням густини полімерної матриці, при дії зовнішнього одновісного тиску, а також під впливом зовнішнього важкого атома брому.