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Study of spectral and luminescence properties and association in hydrocarbon solvents of stilbene and distyrylbenzene derivatives

V.M.Shershukov, A.I.Bedryk, A.O.Doroshenko

Institute for Scintillation Materials, STC "Institute for Single Crystals," National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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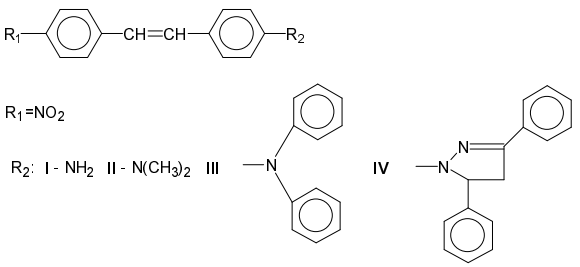
Spectral and luminescence properties and association of stilbene and distyrylbenzene derivatives in hydrocarbon solvents have been studied. The bulky triphenyl amine group being a strong electron donor introduced in those molecules has been shown to make it possible to obtain efficient yellow-green organic luminophors not inclined to association.

Проведен синтез новых производных стильбена и 1,4-дистирилбензола, исследованы их спектрально-люминесцентные свойства и ассоциация в растворах углеводородных растворителей. Показано, что введение в молекулы этих соединений в качестве заместителей объемной сильной электронодонорной группы трифениламина позволяет получить эффективные органические люминофоры желто-зеленого свечения, не склонные к ассоциации.

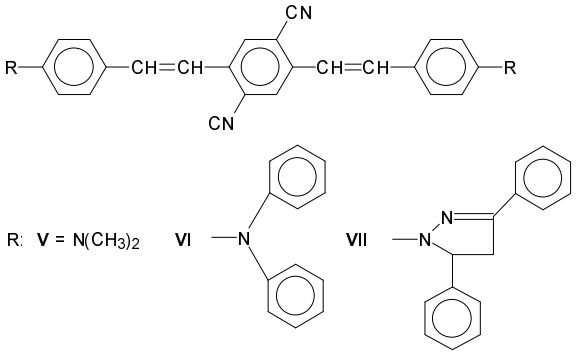
Association of complex organic molecules is under intense investigation at present [1–3]. This is caused both by the scientific interest in the nature of excited electron states and the part played thereby in chemical and biological processes, photochemical reactions, etc., and by the wide application of organic dyes in scintillation and laser engineering, as light guides, emission converters, in solar power engineering (as solar emission concentrators), as well in other branches. In all the above cases, a luminophor is used either in the form of liquid or solid solution or as a vacuum-sprayed film. To attain a maximum efficiency of any scintillating, laser, or light-converting material, it is necessary, on the one hand, to provide a complete incident light absorption making use of the luminophor concentration; on the other hand, to prevent a luminescence intensity decrease and a considerable red shift thereof due to formation of associates. The luminescence quenching at high concentrations of an organic luminophor is due to resonance transfer of the electron excitation from one monomer dye molecule to another identical molecule. Some of such transitions are accompanied by quenching. The quenching was supposed to be also possible when the energy is transferred between distant molecules, but the excitation quenching probability at the migration increases more swiftly than that of quenching-free transfer as the distance diminishes. Thus, the molecular arrangement in solution or in solid state is of importance in the probability variation of non-radiative transitions.

The triphenyl amine is in our opinion among the structures of good promise. First, the moiety is of propeller-like structure (the angles between the nitrogen atom and phenyl rings amount about 30°) that hinders considerably the close molecular packing in various aggregate states. Second, it is a strong electron donor and, therefore, makes it possible to vary widely the absorption and emission spectral ranges of the luminophors being developed. Bearing in mind those circumstances, we have synthesized the stilbene derivatives (I, II, III, IV)

and distyrylbenzene ones (V, VI, VII) as efficient organic luminophors of a wide practical application. The compounds combine in their structures both electron donors (including triethyl amine group) and strong electron acceptors (nitro group in the stilbene derivatives and cyano group in the distyrylbenzene ones). In the case of stilbene,



While in the case of distyryl benzene,



To elucidate the diarylamino group effect on the spectral characteristics of organic compounds containing it as a substituent, we have carried out the quantum-chemical calculations for a series of model molecules — *p*-nitrostilbene derivatives (Compounds I, II, III, IV). The electron-donating characteristics of substituting moieties introduced in the nitrostilbene molecule will depend considerably on the configuration of nitrogen atom through which the moieties are attached to the parent molecule. To elucidate that problem, the calculations have been carried out for Compounds I through IV with the full geometry optimization within the frame of AM1 method [4]. Some results are presented in Table 1.

The main geometry parameters are as follows: the rotation angle of the introduced moiety with respect to the plane of the nearest benzene ring (dihedral angle θ_{TICT}) and the pyramidality extent of the nitrogen atom (valence angle θ_{pyr}) that has been evaluated as the average angle between its single bonds. Basing on the latter characteristic, it is possible to estimate the relative fraction of sp^2/sp^3 boundary hybridized states for the atom by comparing the θ_{pyr} value with the limiting values for sp^2 and sp^3 states (120° and 109.1°, respectively). Moreover, the Table comprises the C–N bond length ($\mathbf{r}_{C-N}$) and order ($\mathbf{p}_{C-N}$) values that characterize also the conjugation of the substituent introduced with the parent nitrostilbene molecule, dipole moments (μ), charges on the nitrogen atom of the substituent (q_N) and total nitro group charges (q_{NO2}) that characterize the electron density redistribution from the substituent to the electron-accepting center in the ground state. As the substituent volume is increased, the C–N bond length is seen to rise and its order to decrease respectively. The turning angle of the substituent with respect to the plane of the nearest benzene ring increases also in the I–IV sequence. At the same time, the nitrogen atom piramidality extent is maximum in amino- and pyrazolinyl-substituted compounds and the electron-donating effect transmission to the nitro group is maximum in the dimethyl amino derivative.

The results obtained for diphenyl amino derivative are of a particular interest. Its nitrogen atom has been found surprisingly to be in the essentially ideal sp^2 hybridized state although the plane passing through the C–N bonds of that substituent forms a 30° angle with the ring plane. As a result of steric hindrances arising in the triphenylamino group, the latted takes a propeller-like configuration with the C–N bonds lying essentially in a single plane. The validity of the calculations carried out is confirmed by the X-ray structure analysis data for com-

Table 1. Quantum-chemical calculation data for **I–IV** molecules in ground state

Comp.	*R*	$\mathbf{r}_{C-N}$, Å	$\mathbf{p}_{C-N}$	$\mathbf{q}_N$	$\mathbf{q}_{NO2}$	μ, D	θ_{TICT}	θ_{Pyr}, °	sp^2, %
I	NH_2	1.392	1.106	−0.336	−0.140	8.07	0°	115.0°	58 %
II	$N(CH_3)_2$	1.403	1.071	−0.262	−0.141	8.58	17°	117.4°	76 %
III	$N(C_6H_5)_2$	1.408	1.014	−0.208	−0.138	7.20	30°	120.0°	100 %
IV	Pyrazolinyl	1.425	1.007	−0.171	−0.130	8.81	23°	115.8°	62 %

Table 2. Characteristics of long-wavelength electron transitions in absorption spectra of Compounds I–IV in vacuum

Comp.	ΔE, eV	ν, cm^{-1}	λ, nm	f_{osc}	$\mu(S_0)$, D	$\mu(S_1)$, D	$\Delta\mu$, D	$\Delta\mu^*$	% CT
I	3.70	29900	334	1.28	8.43	18.33	9.97	18.89	42 %
II	3.65	29400	340	1.30	8.63	19.39	10.80	21.37	47 %
III	3.41	27500	363	1.20	7.46	18.63	11.18	29.13	65 %
IV	3.55	28600	349	1.68	10.56	16.90	6.53	17.86	40 %

Table 3. Quantum-chemical estimations of solvate-induced shifts in electron absorption spectra of Compounds I–IV

Comp.	R	a, Å	Toluene, cm^{-1}	Ethanol, cm^{-1}
I	NH_2	7.0	−2700	−4600
II	$N(CH_3)_2$	7.5	−2500	−4200
III	$N(C_6H_5)_2$	8.5	−1600	−2700
IV	Pyrazolinyl	9.5	−700	−1400

pounds of similar structures [5]. The electron density decrease at the nitrogen atom of the substituent in the I–IV sequence reflects its delocalization to the moieties attached thereto. Thus, in the diphenyl-amino derivative, the conjugation between the nitrogen atom lone electron pair in the substituent and the molecular π-system is weakened due to the steric hindrances although its predominant sp^2 hybridized state allows to expect the conjugation recovery under the possible conformational re-building in an excited state [6, 7].

The electron absorption spectra of Compounds I–IV have been calculated under the INDO/S approximation using the oxygen atom parameter system modified with the aim to calculate correctly the $n\pi$-state energy values [8]. The calculated spectral characteristics are summarized in Table 2 where $\Delta\mu^*$ is the dipole moment change under electron excitation associated only with the electron density shift from the donating to accepting molecular fragment. Basing on that quantity, the charge transfer extent can be estimated when the nitrogen atom of the substituted amino group (nitrogen atom 1 of the pyrazoline ring) is considered as the electron excess center and the amino group nitrogen atom, as the electron-depleted center.

It is seen from the calculated results that all the compounds under consideration are characterized by a substantial electron density redistribution under excitation that is reflected in a considerable dipole moment increase in the S_1 state. The charge transfer extent in the amino and dimethyl-amino derivatives can be estimated as 42–47 % while it attains 65 % in the diphenyl-amino one. This fact indicates that the benzene rings attached to the nitrogen atom are involved in the total molecule electron excitation; a fraction of the electron density concentrated in the π systems is transferred to the nitrogen atom, thus increasing its electron-donating properties. In contrast, in the pyrazoline derivative IV, the excess electron density of the nitrogen atom 1 is redistributed not only towards the nitro group but also to the pyrazoline ring and the benzene ring attached thereto in the 3 position. Thus, the electron-donating properties of the pyrazoline substituent must be somewhat decreased as compares to the other model molecules, as it results from the above calculation.

The solvent effect on the electron absorption spectra of the model molecules has been estimated according to [9]. The approach is based on the solvatochromic dependences by Bilot and Kavsky relating the solvent macroscopic parameters with the polar and structure parameters of the excited and unexcited solute molecule:

$$\Delta\nu_a = -m_3\frac{2n^2+1}{n^2+1}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)-m_2\frac{3(n^4-1)}{2(n^2+2)^2}. \quad (1)$$

Here m_2 and m_3 are parameters depending on the solute properties: dipole moments in the ground and excited states (μ_0 and μ_1) as well as the radius of spherical Onsager void occupied by the molecule in the solvent volume:

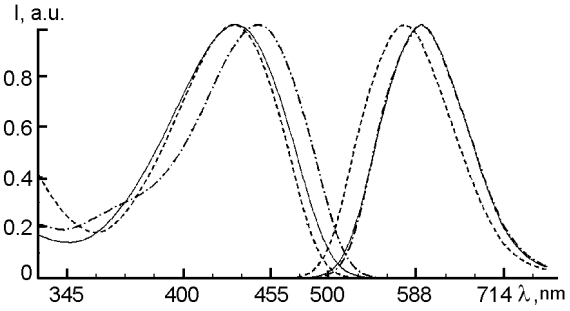


Fig. 1. Absorption and fluorescence spectra of substituted nitrostilbenes in toluene: II (solid line), III (dashed line), IV (dot-and-dashed line).

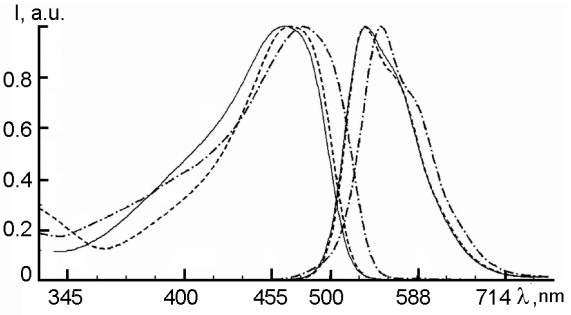


Fig. 2. Absorption and fluorescence spectra of substituted substituted distyrylbenzenes in toluene: V (solid line), VI (dashed line), VII (dot-and-dashed line).

$$m_2 = \frac{2(\mu_1^2 - \mu_0^2)}{hca^3},\ m_3 = \frac{2\mu_0(\mu_1 - \mu_0)}{hca^3}. \qquad (2)$$

Substituting the calculated polar (Table 1) and structure (Table 2) characteristics of the molecules being considered into (1), it is possible to estimate the solvate-induced shifts when passing from vacuum (data from Table 2) to solutions (Table 3 presents the results for toluene and ethanol; for other solvents, the estimations can be obtained in a similar manner). The largest changes in the electron absorption spectra are to be expected for amino and dialkylamino substituents. The solvate effects should be somewhat smaller in diphenylamino derivative and in pyrazolinyl-containing molecules, the smallest. At the same time, it is noteworthy that the above estimations have been done without taking into account the possible conformation changes of the molecules under excitation while those changes may contribute substantially enough to the experimental changes of spectral characteristics [7]. The above theoretical estimations were checked in experiment taking the I–IV derivatives as examples as well as using the distyrylbenzene derivatives (V, VI, VII) containing similar electron-donating groups. The spectral properties thereof were studied in toluene. The representative spectra are presented in Figs. 1 and 2 and the numerical results are summarized in Table 4.

It follows from the results obtained that in spite of the presence of the electron-accepting nitro group, the nitrostilbenes studied exhibit an intense fluorescence. In this case, the triplet $n\pi^*$ levels of the nitro group have a higher energy than the lower singlet excited state of the molecules and thus cannot influence negatively the spectral characteristics. The increased extinction coefficient of Compound III as compared to II confirms the above conclusion on the involvement of benzene rings attached to the nitrogen atom in the conjugation with the molecular π system. The pyrazoline derivative exhibits an even more increased extinction coefficient that reflects the inclusion of 3-phenyl substituted pyrazoline ring into the total conjugated molecular system of Compound IV. At the same time, the diphenyl nitrostilbene derivative shows fluorescence in somewhat shorter-wave region than its dimethyl-amino analog and the longest emission wavelength is observed at the pyrazolinyl substituted compound. The Stokes fluorescence shifts decrease in the sequence I–IV in full accordance with conclusion on the manifestation character of solvatochromic effects in the series of substituted nitrostilbenes. As to distyrylbenzene derivatives, the properties of the considered substituents are manifested themselves in a substantially identical manner, except for an increased involvement of diphenyl-amino group benzene rings in the conjugation. In absorption spectra of Compound V the electron transition band 1 is more intense and shifted somewhat towards longer wavelengths as compared to VI. The studied distyrylbenzene derivatives are characterized by much lower Stokes shifts as compared to the above-considered nitrostilbene ones. This points to a substantially lesser importance of solvate and structure relaxation in those molecules. That fact seems to be quite natural if the symmetrical structures of V–VII are taken into account.

The spectral and luminescence characteristics have been studied for toluene solutions of one synthesized luminophor, 4-nitro-4′-diphenylaminostilbene (III) and, for comparison sake, of its analogue, 4-dimethylamino substituted compound (II). Or-

Table 4. Spectral characteristics of substituted nitrostilbenes and distyrylbenzenes in toluene

Comp.	R	ν_a	λ_a	ε_a	ν_f	λ_f	$\Delta\nu_{ST}$	φ_f
Nitrostilbenes								
II	$N(CH_3)_2$	23220	431	22300	16840	594	6380	0.49
III	$N(C_6H_5)_2$	23280	430	28400	17420	574	5860	0.56
IV	Pyrazolinyl	22440	446	39200	16820	595	5620	0.50
Distyrylbenzenes								
V	$N(CH_3)_2$	21560	464	45800	18780	532	2780	0.37
VI	$N(C_6H_5)_2$	23160	468	60200	18800	532	2560	0.51
VII	Pyrazolinyl	20920	478	no dis.	18240	548	2680	0.45

ganic molecules are known to form associates in the ground state due to weak Van-der-Waals interactions. Since the molecules under study contain no functional groups capable of coordination bonds formation with each other, the specific interactions of other nature can be neglected. The formation of Van-der-Waals associates must result in distortions (blurring, widening) of absorption spectra. However, the experimental electron absorption spectra of Compounds II and III show the shape constancy up to concentrations of (3 to 6)$\cdot 10^{-3}$ mol/L, thus, such interactions can be excluded, too, or the saturated solution concentrations should be provided to record them. The association in excited state may result in fluorescent or non-fluorescent products. In the first case, those are excimers (excited dimers) showing a fluorescence as a wide structureless emission band localized in a longer-wavelength spectral region than the monomolecular compound spectrum. As to Compound III, neither widening nor shifting of its luminescence band is observed. Thus, the formation of excimer-like fluorescent associates can be excluded to a high probability.

The formation of non-fluorescent associates does not influence the shape of absorption and emission spectra and can be discovered only basing on the fluorescence lifetime variation as the luminophor concentration rises. When there is no association (at low concentrations), the luminophor reciprocal lifetime is the sum of rate constants of radiative and non-radiative processes resulting in deactivation of its electron-excited molecules:

Table 5. Physical properties and analytical data for compounds I–VII

Comp.	Formula	M.p.(°C)	Yield , %	Elemental analysis (calculated/found)		
				C	H	N
I	$C_{14}H_{12}N_2O_2$	228	20	70.05	4.98	11.68
				70.03	4.99	11.66
II	$C_{16}H_{16}N_2O_4$	251	25	71.65	6.00	10.40
				71.67	5.98	10.42
III	$C_{26}H_{20}N_2O_2$	143	28	79.62	5.12	7.16
				79.60	5.14	7.18
IV	$C_{29}H_{22}N_3O_2$	199	19	78.40	5.00	9.44
				78.38	4.98	9.46
V	$C_{28}H_{26}N_4$	300	51	80.40	6.25	13.44
				80.41	6.23	13.42
VI	$C_{48}H_{34}N_4$	242	60	86.50	5.12	8.43
				86.47	5.09	8.41
VII	$C_{54}H_{38}N_6$	258	48	84.18	4.97	10.92
				84.16	4.95	10.88

$$\frac{1}{\tau_a} = rf + rd.$$

As the associates are formed, that expression should be supplemented by the association rate

$$\frac{1}{\tau_a} = rf + rd + r_{ass}.$$

In this case, the luminophor lifetime must drop in concentrated solutions. This phenomenon is often referred to as "the luminescence concentration quenching", although the luminescence weakening at high concentrations is due also to various other mechanisms.

To check that possibility, we have studied the lifetime of dimethylamino- (II) and diphenylamino-(III) substituted nitrostilbenes within a wide concentration range (10^{-5} to $6{\cdot}10^{-3}$ mol/L). The study results are presented in Fig. 3 where the fluorescence quenching functions after Schroeder-Volmer are built. From the slopes of the straight lines obtained, the association constants in excited state can be calculated as

$$A^* + A \xrightarrow{r_{ass}} A^*_2.$$

Form the kinetic experiment data, the rate constants of concentration quenching (k_Q, $L{\cdot}mol^{-1}{\cdot}c^{-1}$) have been calculated to amount $1.60{\cdot}10^{10}$ for $-N(CH_3)_2$ and $2.56{\cdot}10^9$ for $-N(C_6H_5)_2$. For compounds containing the diphenylamino group, the constant coincides essentially with the rate constant of diffusion-controlled processes. Thus, introduction of the bulky diphenylamino group into stilbene molecule, thus hindering the mutual approach of two molecules, results in the association constant decrease by a factor of almost 6.

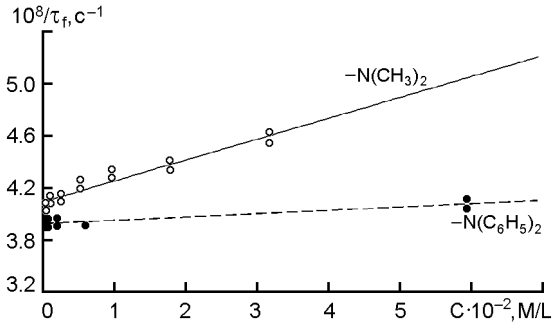


Fig. 3. Concentration dependence of reciprocal lifetime.

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Дослідження спектрально-люмінесцентних властивостей та асоціації у розчинах вуглецеводневих розчинників похідних стильбену та дистирилбензолу.

В.М.Шершуков, О.І.Бедрик, А.О.Дорошенко

Проведено синтез нових похідних стильбену та 1,4-дистирилбензолу, досліджено їх спектрально-люмінесцентні властивості та асоціацію у розчинах вуглецеводневих розчинників. Показано, що введення у молекули цих сполук в якості замісників об'ємної сильної електронодонорної групи трифеніламіну дозволяє синтезувати ефективні органічні люмінофори жовто-зеленого світіння, не схильні до асоціації.