RESEARCH IN THE 2,5-DIARYL-1,3,4-OXADIAZOLE SERIES.
2.* ELECTRONIC STRUCTURES AND SPECTRAL-LUMINESCENCE PROPERTIES OF 4-NITRO-4'-DIMETHYLAMINO-SUBSTITUTED 2,5-DIPHENYL-1,3,4-OXADIAZOLES, trans-STILBENES, AND p-TERPHENYLS

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The dependence of the spectral-luminescence properties of compounds of the $O_2N{-}C_6H_4{-}M{-}C_6H_4N(CH_3)_2$ type on the electronic nature of bridge M was studied. Quantum-chemical calculations of the absorption spectra and electron-density distributions of substituted trans-stilbenes, p-terphenyls, and 2,5-diphenyl-1,3,4-oxadiazoles were made by the Pariser–Parr–Pople (PPP) method. The results of theoretical and experimental studies constitute evidence that the conductivity of the electronic effects in the 2,5-diphenyl-1,3,4-oxadiazole system is similar to that in the p-terphenyl system.

In a previous paper [1] we investigated the spectral-luminescence properties and dipole moments of a number of substituted 2,5-diphenyl-1,3,4-oxadiazoles (PPD). The experimental data obtained constitute evidence for rather effective transmission of the electronic effects through the oxadiazole ring. It seemed of interest to compare the PPD system, in which the bridge is an oxadiazole ring, with the p-terphenyl and trans-stilbene systems, which have electron transitions of the same nature and contain bridged groupings (phenylene and ethylene) with known conductivities of the electronic effects.

The regularities in the change in the position of the absorption maximum when one or two substituents with the same electronic nature are introduced into PPD are similar to those previously observed in a study of substituted stilbenes [2], which once again confirms the π,π^* nature of the long-wave absorption band of diaryloxadiazoles. The introduction of a dimethylamino group in the para position of the second phenyl ring in the 4-nitrostilbene (λ_{max} = 326 nm) and 2-(p-nitrophenyl)-5-phenyl-1,3,4-oxadiazole (λ_{max} = 317 nm) molecules leads to bathochromic shifts of 106 and 73 nm, respectively (Table 1). Thus the electronic effects of substituents in the PPD system are transmitted more poorly than in the analogous trans-stilbene derivatives.

The absorption maximum of the long-wave band of 4-nitro-p-terphenyl lies at 316 nm [3], and the bathochromic shift when a dimethylamino group is introduced in the 4 position is 69 nm (Table 1). This is in agreement with the data on the poorer conductivity of the phenylene bridge as compared with the ethylene bridge [4, 5]. The results make it possible to assume that the conductivity of the electronic effects in the PPD system is close to the conductivity in p-terphenyl.

The fact that the absorption spectra of 4,4'-disubstituted trans-stilbenes, p-terphenyls, and PPD with two substituents with the same electronic nature are similar to one another is interesting (Fig. 1). At the same time, the spectra of analogous compounds with substituents with different electronic natures differ (Fig. 2); this is evidently primarily due to the

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*See [1] for communication I.

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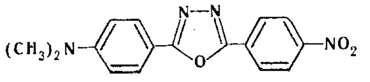
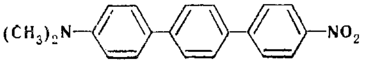
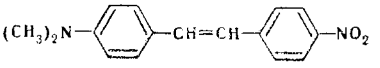
TABLE 1. Spectral Characteristics of Substituted 2,5-Diphenyl-1,3,4-oxadiazoles, p-Terphenyls, and trans-Stilbenes in Toluene

Compound	Absorption		Luminescence		Δν, cm-1	$k_f \cdot 10^{-8}$ sec-1
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η		
	307 390	3,08 1,22	565	0,15	7900	5,32
	295 385	Varies	575	0,25	8550	
	300 432	1,20 2,28	580	0,7	5800	8,48

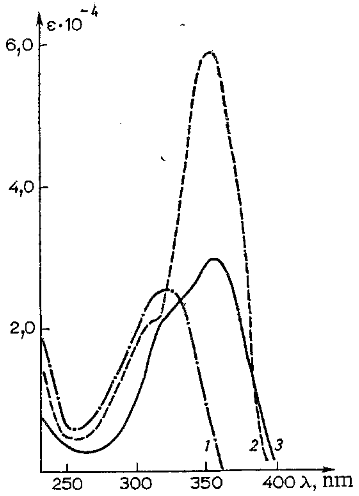


Fig. 1

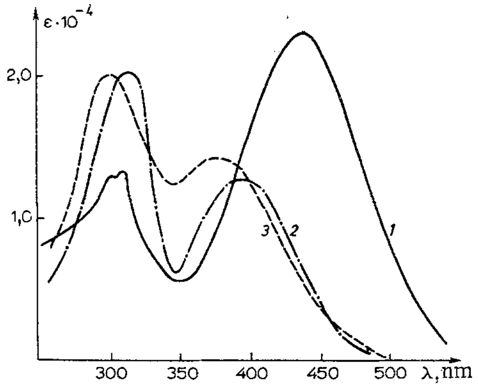


Fig. 2

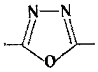
Fig. 1. Absorption spectra of 4-amino-4"-dimethylamino-p-terphenyl (1), 2,5-bis(p-dimethylaminophenyl)-1,3,4-oxidiazole (2), and 4-amino-4'-dimethylamino-trans-stilbene (3) in ethanol.

Fig. 2. Absorption spectra of 4-nitro-4'-dimethylamino-substituted trans-stilbene (1), p-terphenyl (2), and 2,5-diphenyl-1,3,4-oxadiazole (3) in chloroform.

electronic nature of the bridge and, possibly, the geometry of the molecules. The long-wave band in the spectra of such substituted trans-stilbenes and p-terphenyls is an intramolecular charge-transfer band [5-7]. If it is assumed that in the case of the oxadiazole derivatives the long-wave band is due to a similar electron transition (Table 2), comparison of their spectra (Fig. 2) makes it possible to conclude that the molar extinction coefficient (i.e., the probability of an electron transition) decreases in the order trans-stilbene > p-terphenyl > PPD. The interaction of the substituents through the π system of the molecules also evidently decreases in the same order. It is presently not possible to unambiguously ascribe this weakening of the interaction to the electronic nature of the heteroring, since exhaustive data on the geometry of PPD are not available. The possibility of the superimposition of these two factors is not excluded.

One's attention is drawn to the large Stokesian shifts (Δν) for nitro-dimethylamino-substituted trans-stilbenes, p-terphenyls, and PPD (Table 1). However, while the fluorescence

TABLE 2. Overall Electron Charges on the Fragments in the Ground and Excited States

p-RC_6H_4—M—C_6H_4R'-p			Overall electron charge									
			S_0					S_1				
M	R	R′	R	C_6H_4	M	$(C_6H_4)'$	R′	R	C_6H_4	M	$(C_6H_4)'$	R′
	H	H		0,007	−0,015	0,007			−0,038	0,076	−0,038	
	H	NH_2		0,001	−0,034	−0,214	0,246		−0,153	−0,121	−0,126	0,401
	NH_2	NH_2	0,243	−0,217	−0,051	−0,217	0,243	0,324	−0,239	−0,170	−0,239	0,324
	H	COOH		0,010	−0,009	0,043	−0,045		0,025	0,160	−0,098	−0,088
	COOH	COOH	−0,044	0,045	−0,004	0,045	−0,044	−0,067	−0,016	0,167	−0,016	−0,067
	NH_2	COOH	0,248	−0,212	−0,029	0,039	−0,047	0,400	−0,076	−0,055	−0,178	−0,097
1,4-C_6H_4	H	H		0,000	0,000	0,000			0,000	0,000	0,000	
	H	NH_2		−0,040	−0,015	−0,163	0,180		−0,086	−0,171	−0,440	0,302
	H	NO_2		0,012	0,014	0,053	−0,078		0,107	0,256	−0,069	−0,303
	NO_2	NH_2	−0,082	0,051	0,002	−0,153	0,184	−0,266	−0,215	0,094	0,105	0,282
CH=CH	H	H		0,000	0,000	0,000			−0,010	0,022	−0,010	
	H	NH_2		−0,011	−0,013	−0,156	0,181		−0,158	−0,093	−0,035	0,280
	H	NO_2		0,016	0,015	0,052	−0,083		0,169	0,170	−0,042	−0,257
	NO_2	NH_2	−0,088	0,043	0,010	−0,141	0,188	−0,283	−0,183	0,056	0,111	0,297

quantum yield for 4-dimethylamino-4'-nitro-stilbene reaches a significant value (η = 0.7), it is considerably lower for the corresponding terphenyl and oxadiazole derivatives. The fluorescence rate constants (k_f) of 4-nitro-4'-dimethylaminostilbene and 2-(p-dimethylaminophenyl)-5-(p-nitrophenyl)-1,3,4-oxadiazole (Table 1) calculated from the absorption spectra [8] differ only slightly, i.e., deactivation of excited state S_1 for substituted PPD is determined by the rates of the nonradiation processes.

We performed quantum-chemical calculations of the absorption spectra and electron density distributions of substituted trans-stilbenes, p-terphenyls, and PPD within the framework of the self-consistent field (SCF) method within the PPP approximation (π approximation) with the aid of the program in [9], which was realized with a BÉSM-4 computer. When substituents are introduced into the PPD molecule, the changes in the electron-density distribution in the ground state (Table 2) are local in character and are extended mainly to the phenyl group in which the substituent is located and then to the heteroring. The changes are insignificant in the second aromatic ring. Significant redistribution of the electron density of the entire molecule occurs upon excitation. A comparison of the changes in the electron-density distribution when substituents are introduced in PPD and in the trans-stilbene and p-terphenyl molecules shows that they are similar in character. However, the changes in the electron density in the phenyl ring when substituents are introduced in the other phenyl ring in trans-stilbene and p-terphenyl are greater than in the case of PPD, and this makes it possible to speak of the poorer conductivity of the electronic effects by the oxadiazole ring as compared with the ethylene and phenylene groupings. This is in agreement with the experimental data on the weakening of the interaction of the substituents through the system in the order stilbene > terphenyl > PPD. It might be assumed that this sort of effect is associated with the electron-acceptor properties of the oxadiazole ring, in contrast to which the ethylene and phenylene groupings may display both electron-donor and electron-acceptor properties (Table 2).

Thus the calculated values obtained, just like the spectral studies, confirm that the long-wave band in the absorption spectra of 2,5-diaryl-substituted 1,3,4-oxadiazole is due to an $S_0 \to S_1$ transition of the π, π^* type and constitutes evidence for conductivity of the electronic effects by the oxadiazole ring.

EXPERIMENTAL

The absorption spectra were recorded with an SF-4 spectrophotometer. The luminescence spectra were recorded with a device consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a DMR-4 monochromator. The absolute luminescence quantum yields of toluene solutions (η) were determined by the equal absorption method.

4-Nitro-4"-dimethylamino-p-terphenyl. A mixture of 3 g (0.01 mole) of 4-nitro-4"-amino-p-terphenyl obtained by the method in [10] and 5 ml (0.05 mole) of dimethyl sulfate was heated at 150-160°C for 1 h, after which it was cooled to room temperature and poured into water. The resulting precipitate was removed by filtration and washed successively with 5%

sodium carbonate solution, water until the wash waters were neutral, and ethanol to give 0.7 g (21%) of a product with mp 319-320°C (from dimethylformamide). Found, %: C 75.2; H 5.8; N 8.6. $C_{20}H_{18}N_2O_2$. Calculated, %: C 75.4; H 5.7; N 8.8.

4-Nitro-4'-dimethylaminostilbene was obtained by the method in [11]; the synthesis of 2-(p-nitrophenyl)-5-(p-dimethylaminophenyl)-1,3,4-oxadiazole was described in [1].

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SYNTHESIS AND REACTIONS OF THIENO[2',3':5,4]THIENO[2,3-c]- AND THIENO[2',3':4,5]THIENO[2,3-c]PYRYLIUM SALTS

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Methods for the synthesis of isomeric thienothiophenes by cyclization of methyl γ-thienylmercaptoacetoacetates in polyphosphoric acid (PPA) were developed. It is shown that the acylation of the acetonyl derivaties of isomeric thienothiophenes in an aliphatic acid anhydride—70% perchloric acid system leads to the corresponding pyrylium salts. Some reactions of the latter with nucleophilic reagents were studied. The structures of the substance obtained were confirmed by the IR and PMR spectra.

In a continuation of our research on the synthesis and properties of pyrylium salts condensed with heterocyclic systems [1-3] we have realized the synthesis of thieno[2',3':5,4]thieno[2,3-c]pyrylium and thieno[2',3':4,5]thieno[2,3-c]pyrylium perchlorates.*

We have observed that 5-alkylthieno[2,3-b]thiophen-3-ylacetic acid esters IIa,b and 5-methylthieno[3,2-b]thiophen-3-ylacetic acid ester IVa (Table 4) are formed in good yields in the intramolecular cyclization of γ-thienylmercaptoacetoacetic acid esters in polyphosphoric acid (PPA). The cyclization takes place under mild conditions only when substituent R is present in one of the α positions of the thiophene ring. Only resinification

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*See [4] for our preliminary communication.

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