ω, ω'-DIHETARYL-SUBSTITUTED 2,5-DIMETHYL-1,4-DIVINYLBENZENES

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A series of ω, ω' -dihetaryl-substituted 2,5-dimethyl-1,4-divinylbenzenes has been synthesized and these show an increased solubility when compared with analogs not containing methyl groups in the central benzene ring. The dependence of spectral parameters on the chemical structure has been analyzed.

Heterocyclic analogs of 1,4-distyrylbenzene are efficient luminophores which find use in quantum electronics, in scintillation technology, as optical whiteners, and in other areas of science and technology [1, 2]. The structural features of these compounds (chain structure, presence of ethylene bonds) lead to poor



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	Yield, %		60	58	90	06 .	80	56	58	62
	luminescence, $\lambda_{max}(\eta)$	DMF	465; 486 (0,33)	I	440; 462 (0,25)	450; 471 (0,33)	440; 465 (0,58)	445; 470 (0,40)	455; 476 (0,62)	435; 460 (0,66)
tronic spectra		toluene	460; 485 (0,35)	445; 473 (0,37)	435; 460 (0,41)	450; 475 (0,45)	445; 470 (qualitative)	455; 480 (0,53)	445; 470 (0,52)	435 (0,53)
Elec	absorption, λ_{max} , (ϵ ·10 ⁻¹)	DMF	413 (7,32)		390 (5,55)	400 (5,67)	394 (6,47)	344 (5,54) 400 (4,35)	386 (4,86)	369 (4,83)
		toluene	415 (7,08)	405 (8,35)	383 (5,49)	385 (4,93)	1	395 (8,03)	383 (6,05)	370 (4,33)
	IR spectrum, cm ^{-I}		1610	1613	1620	1618	1630	1625	1628	1617
9			951	959	965	963	970	956	696	957
	mp, °C		255	270	257	276	230	259	262	278
		CI	<u>15,32</u> 15,46	<u>14,25</u> 14,46			1		1	ł
	%	S	l	<u>12,93</u> 13,03		<u>14,81</u> 15,09			ļ	
Found. %	Calculated,	z	l	Ι	7,13	<u>6,38</u> 6,60	<u>14,25</u> 14,35	<u>4,41</u> 4,69	<u>9,13</u>	7, <u>42</u> 7,50
		Н	<u>4,21</u> 4,35	<u>4,15</u> 4,06	<u>4,91</u> 5,10	<u>4,39</u> 4,69	<u>5,40</u> 5,46	<u>5,38</u> 5,38	<u>5,00</u>	<u>5,42</u> 5,63
		С	<u>73,20</u> 73,20	<u>68,15</u> 68,43	<u>79,34</u> 79,59	73,58	<u>29,90</u> 80,00	<u>84,36</u> 84,56	<u>80,08</u> 80,26	<u>86,70</u> 86,86
	Empírical formula		C ₂₈ H ₂₀ Cl ₂ O ₂	C28H20Cl2S2	C ₂₆ H ₂₀ N ₂ O ₂	C26H20N2S2	C ₁₆ H ₂₂ N4	C42H32N2O2	C40H30N4O2	C ₅₁ H ₁₂ N ₄
	Com- pound		VIa	VIb	VIc	PIA	Vle	VIF	VIg	٩IJ

vinylbenzenes
·I,4-div
5-Dimethyl-
I Substituted 2,
or ω,ω'-Hetary
Characteristics fc
l Luminescent (
1. Spectra
TABLE

photostability and low solubility. In addition, it is known that the introduction of alkyl substituents into the central benzene ring leads to an increase not only in solubility but also in photostability [3]. With this in mind, we have synthesized various ω, ω' -dihetaryl-substituted 1,4-divinylbenzenes VIa-h containing two methyl groups in the central benzene ring. These compounds have been obtained by different methods depending on the reactivity of the carbonyl and methylene components in the starting materials which, in their turn, were determined by the structure and electronic nature of the heterocycles. Hence compounds VIc-e were prepared by condensation of 2,5-dimethylterephthalaldehyde (I) and the corresponding methyl substituted II in superbase medium [4] and VIa,b,f-h were synthesized by a Horner reaction [5]. However, for the synthesis of VIf 2,5-dimethylterephthalaldehyde (I) and 2-(4'-bromomethylphenyl)-5-phenyloxazole (III) were used and, for the rest, the heteroaromatic aldehyde and 2,5-dimethyl-1,4-dibromomethylbenzene (IV).

The IR spectra of the synthesized compounds showed the presence of strong bands in the region 950-970 cm⁻¹ due to the out of plane deformation vibrations of the γ CH *trans* ethylene group. The stretching bands for the double bonds at 1610-1630 cm⁻¹ are of low intensity which corresponds to systems with a low polarized double bond [6].

The spectro-luminescence parameters of the obtained compounds have also been studied using toluene and DMF solvents (Table 1). Analysis has shown that the spectral absorption and fluorescence are characteristic of related analogs not containing methyl groups [4], but having lower extinction coefficients (from 79,000 for 1,4-di(benzoxazolyl-2-vinyl)benzene to 54,000 for compound VIc) and this is caused by the steric hindrance of methyl groups. However, disturbance to the coplanarity of the molecule is evidently small since all the characteristics of the electronic transition responsible for the fluorescence (with the exclusion of the intensity) are virtually unchanged when compared to those analogs not containing the methyl groups. The absence of a marked solvatochromic or solvatofluorochromic effect when changing from toluene to DMF points to a weak polarity in the symmetrical structure of the molecule and the small observed changes are cause by the varying polarizability of the ground and excited state in the heterocycles.

Study of the solubility of the compounds obtained in toluene solvent has shown that it is significantly higher than their analogs and this agrees with the lowering of their melting points. Thus, for example, the solubility of compound IVc is twice that of 1,4-di(benzoxazolyl-2-vinyl)benzene and their melting points are 257 and 333°C respectively [3].

Hence the introduction of methyl groups into the central benzene ring has almost no effect on the π -electronic system in the molecule but leads to a lowering of the melting point and increase in solubility and this broadens the scope for the practical uses of these compounds.

EXPERIMENTAL

IR Spectra were recorded on a Specord IR-75 instrument for KBr tablets (2% by mass). Absorption spectra were measured on a Specord M-40 instrument and luminescence spectra on a Hitachi-850 spectrophotometer.

2,5-Dimethyl-1,4-di(vinylbenzoxazol-2-yl)benzene (VIc). A solution of 2,5-dimethylterephthalaldehyde I (1.34 g, 0.01 mol) in DMF (20 ml) was added dropwise with stirring to a solution of 2-methylbenzoxazole IIc (3.99 g, 0.03 mol) and powdered KOH (4.48 g, 0.08 mol) in dry DMF (40 ml). The mixture was stirred at room temperature for 1 h, after which HCl (10%) was added with cooling in ice until the reaction was weakly acidic. The precipitate was filtered off, washed with water to neutrality, then with ethanol (15 ml), and dried. Yield 3.27 g (90%); mp 257°C (toluene). Found, %: N 7.00. $C_{26}H_{20}N_2O_2$. Calculated, %: N 7.14.

Compounds VId and VIe were prepared similarly (see Table 1).

1,4-Di(diethylmethylenephosphonato)2,5-dimethylbenzene. A mixture of 1,4-dibromomethyl-2,5-dimethylbenzene IV (2.92 g, 0.01 mol), triethylphosphite (3.32 g, 0.01 mol), and dry *p*-xylene (30 ml) was refluxed for 6 h. *p*-Xylene was distilled off from the reaction product at a residual pressure of 40-50 mm Hg. The phosphonate remaining after distillation was a light yellow oil. Yield 3.25 g (80%).

 $1,4-[\omega,\omega'-Di(3-chlorobenzofuran-2-yl]-2,5-dimethyldivinylbenzene (VIa). A solution of sodium methylate, prepared by dissolving sodium (0.6 g, 0.026 mol) in methanol (15 ml) was added to a solution of$

1,4-[di(diethylmethylenephosphonato)]-2,5-dimethylbenzene (4.06 g, 0.01 mol) in DMF (50 ml). The mixture was held at room temperature for 10 min and a solution of 3-chloro-2-formylbenzofuran Va (3.61 g, 0.02 mol) in DMF (10 ml) was added. The reaction mixture was stirred and left for 15 h. The yellow precipitate was filtered off and an additional amount of the product was separated from the filtrate with water. Yield 2.75 g (60%); mp 255°C (toluene). Found, %: Cl 15.28. $C_{28}H_{20}Cl_2O_2$. Calculated, %: Cl 15.45.

Compounds VIb, f, g, h were obtained similarly (see Table 1).

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