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Synthesis, visible absorption spectra and application properties of disperse dyes derived from 1-indanylidenemalononitrile

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Abstract

The series of dyes derived from 1-indanylidenemalononitrile were prepared and characterised. The purity of the dyes was checked by TLC and elemental analysis; the structure of substances was confirmed by ^{1}H and ^{13}C NMR spectra. The relationships among the structure of dyes, their absorption characteristics and the polarity of a solvent were investigated. The full optimised geometry was computed by AM1 method, the theoretical characteristics of electronic transitions were studied by PPP-MO, CNDO/S and INDO/S procedures. Due to possible application of the studied dyes in textile practice, the colouristic characteristics were determined as well. © 2002 Published by Elsevier Science Ltd.

Keywords: Indanylidenemalononitrile; Disperse dyes; Synthesis; Electronic absorbtion spectra; Colouristic characteristics; Quantum chemical calculation

1. Introduction

Azo dyes form the most important class of organic dyes. But from the point of view of cancerogenicity, they are suspect. Therefore, the research of dyes is aimed at a development of new types of chromophores.

The majority of commercial dyes are based on donor–acceptor chromogenes, i.e. the system consists of electron-donating (D) and electron-accepting groups (A) connected together in conjugation by an unsaturated bridge. D–A charge transfer is responsible for the colour of a dye. The donor part is represented by a π-donor substituent (NR_2, OR), and the acceptor part consists of a more or less delocalized π-system (carbonyl, nitro group, unsaturated bonds with electronegative substituents).

By choosing appropriate π-donor and acceptor groups and the size of the conjugated chain, the dyes can be prepared so that they absorb anywhere in the visible region.

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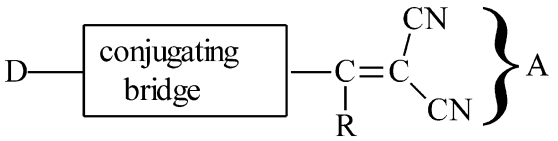
One of the mentioned types is the system:



where dicyanoethylene is one of the strongest π-electron acceptors.

The condensation of malononitrile with aliphatic and aromatic aldehydes and ketones gives colourless or only yellow substances [1,2].

The condensation of 1-indanone with different aldehydes was described for example by Coppens and coworkers [3] and Orlov and co-workers [4].

In this paper, we present the synthesis and the spectral and colouristic characteristics of the series of dyes arising by condensation of 1-indanylidenemalononitrile with benzaldehyde derivatives. These systems have been described recently by Asiri [5] but the synthetic procedure of dyes, their melting points and spectral characteristics published in cited paper, differ dramatically from those presented in this work.

2. Experimental

2.1. Synthesis of dyes (general procedure)

1-Indanylidenemalononitrile (**1**) was prepared by condensation of 1-indanone with malononitrile by the standard procedure [6].

Equivalent quantities of an aromatic aldehyde and the substance **1** were dissolved in warm toluene or cyclohexane and a few drops of piperidine was added with stirring. After adding piperidine, the reaction mixture becomes reddish. Within about 5 min, the product started to precipitate in crystalline form. After refluxing for 1–3 h, the mixture was cooled and a solid product isolated. Recrystallisation from the same solvents yielded long needles.

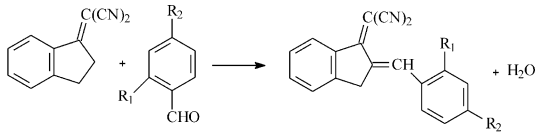
2.2. Elemental analysis and spectral measurements

The ^{1}H and ^{13}C NMR spectra were recorded on an AMX 360 (Bruker) spectrometer (360.13 or 90,56 MHz) using $CDCl_3$, DMSO-d_6, C_6D_6 and acetone-d_6 as solvents. Electronic absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. Used solvents, i.e. acetonitrile, dibutylethere, ethylacetate and methanol, were of spectroscopic grade.

3. Results and discussion

3.1. Synthesis of the dyes

The synthesis proceeded according to the following scheme:



1 **2** a-h

By the condensation **1** with different benzaldehyde derivatives either in cyclohexane or in toluene and in presence of piperidine, the series of new dyes of different shades were prepared; the list of compounds is presented in Table 1.

Table 1
List of prepared compounds (**2**)

Compound (**2**)	R_1	R_2	Solvent	Reaction time (h)	Yield (%)	M.p. (°C)
a	H	H	Cyclohexane	1	74	175–177
b	H	Cl	Cyclohexane	1	77	283–285
c	H	CH_3	Cyclohexane	1.5	85	196–201
d	H	OCH_3	Cyclohexane	2	81	180–182
e	H	C_6H_5	Cyclohexane	1	73	293–295
f	H	$N(CH_3)_2$	Toluene	2	72	295–297
g	H	$N(C_2H_5)_2$	Toluene	1.5	82	241–243
h	CH_3	$N(C_6H_{13})_2$	Toluene	3	71	142–145

The purity of the compounds (**2**) was checked by TLC and verify by elemental analysis. The results in Table 2 show relatively good agreement between calculated and found values.

3.2. ^{1}H and ^{13}C NMR spectra

To confirm the structure of the compounds, the model substance **2f** was studied by ^{1}H and ^{13}C NMR spectroscopy.

The sample was measured in $CDCl_3$, DMSO-d_6, C_6D_6 and acetone-d_6. The best solubility of sample was in deuteriochloroform, but in area of about 7,45 ppm, the overlap of protons H(4), H(5) a H(13) took place. In DMSO-d_6 only two signals [H(4) and H(5)] coincide, as to resolution, the best solvent was hexadeuterobenzene. But the substance has extremely low solubility in this solvent. On the basis of combination of the results in different solvents, the constitution of sample was confirmed. The values of ^{1}H and ^{13}C chemical shifts are presented in Tables 3 and 4.

Table 2
Elemental analysis of compounds (**2**)

Compound (**2**)	R_1	R_2	Formula	Calc. (%)	Found
a	H	H	$C_{19}HO_{12}N_2$	C 85.05	C 84.59
				H 4.51	H 4.51
				N 10.44	N 10.99
b	H	C_6H_5l	$C_{25}H_{16}N_2$	C 87.18	C 86.55
				H 4.68	H 4.82
				N 8.13	N 8.82
c	H	CH_3	$C_{20}H_{14}N_2$	C 85.08	C 84.67
				H 5.00	H 5.05
				N 9.92	N 10.52
d	H	OCH_3	$C_{20}H_{14}N_2O$	C 80.52	C 80.11
				H 4.73	H 4.74
				N 9.39	N 10.01
f	H	$N(CH_3)_2$	$C_{21}H_{17}N_3$	C 81.04	C 80.24
				H 5.46	H 5.44
				N 13.50	N 13.91
g	H	$N(C_2H_5)_2$	$C_{23}H_{21}N_3$	C 81.38	C 81.75
				H 6.24	H 6.05
				N 12.38	N 12.16
h	CH_3	$N(C_6H_{13})_2$	$C_{32}H_{39}N_3$	C 82.59	C 81.42
				H 8.38	H 8.37
				N 9.03	N 8.78

The presence of one methylene group was proved unambiguously.

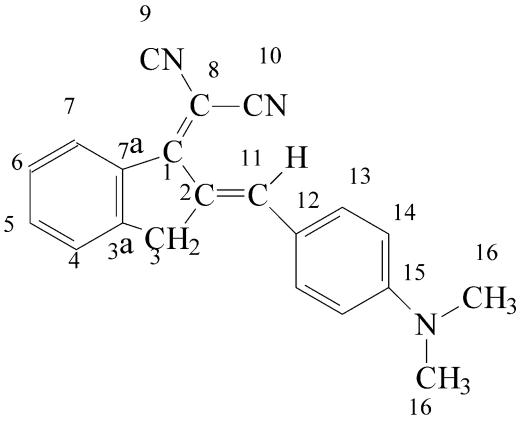
The ^{1}H and ^{13}C chemical shifts were assigned on the basis of interpretation of H,H-COSY, NOESY, gs H,C-HMQC a gs H,C-HMBC two-dimensional spectra.

Table 3
^{1}H and ^{13}C chemical shifts for compound **2f** in hexadeuteriodimethylesulfoxide

H/C	δ (^{1}H)	δ (^{13}C)	NOESY	gs-HMBC
1	–	166.59		H(3), H(11)
2	–	130.95		H(3)
3	4.13	37.41	H(4)	
3a	–	148.03		H(3), H(5), H(7)
4	7.72	125.91	H(3)	
5	7.72	133.93		
6	7.57	127.95	H(7)	
7	8.46	124.47	H(6)	
7a	–	136.71		
8	–	62.49		
9,10	–	116.89 116.42		
11	8.28	138.63	H(13)	H(13)
12	–	122.17		H(14)
13	7.64	133.76	H(11), H(14)	H(11), H(13)
14	6,89	112.31	H(13), H(16)	H(14)
15	–	152.09		H(13), H(16)
16	3.12	39.73	H(14)	

Table 4
^{1}H and ^{13}C chemical shifts for compound **2f** in hexadeuteriobenzene

H/C	δ (^{1}H)	δ (^{13}C)	NOESY	gs-HMBC
1	–	166.49		H(3), H(11)
2	–	132.09		H(3)
3	3.32	37.99	H(4)	
3a	–	147.53		H(3), H(5), H(7)
4	6.87	125.29	H(3), H(5)	
5	7.02	133.39		H(7)
6	6.92	127.76	H(7)	H(4)
7	8.75	126.45	H(6)	H(5)
7a	–	138.27		H(3), H(4)
8	–	67.49		
9,10	–	117.23, 116.82		
11	8.45	138.63	H(13)	H(13)
12	–	124.38		H(14)
13	7.31	133.96	H(11), H(14)	H(11), H(13)
14	6.36	112.64	H(13), H(16)	H(14)
15	–	152.06		H(13), H(16)
16	2.38	39.81	H(14)	



To determine the constitution and isomerism on double bond C(2)=C(11), the following most important interaction through space was determined from 2D NOESY spectra:

H(3)/H(13), H(11)/H(13) and H(14)/H(16). Since no interaction of H(3)/H(11) was observed, the protons H(3) and H(11) are not sterically close one to another. Thus, the orientation of substituents on double bond C(2)=C(11) corresponds to that presented in structural formula.

3.3. Absorption spectra

The replacement of hydrogen atom (R_2 = H) by different electron-donating groups shows characteristic bathochromic shift of the first absorption band (Table 5 and Figs. 1–3).

To investigate the influence of solvents on the colour of dyes, the absorption spectra of substances **2c**, **2d** and **2f** were measured in addition in methanol, in dibutyl ether and in ethyl acetate

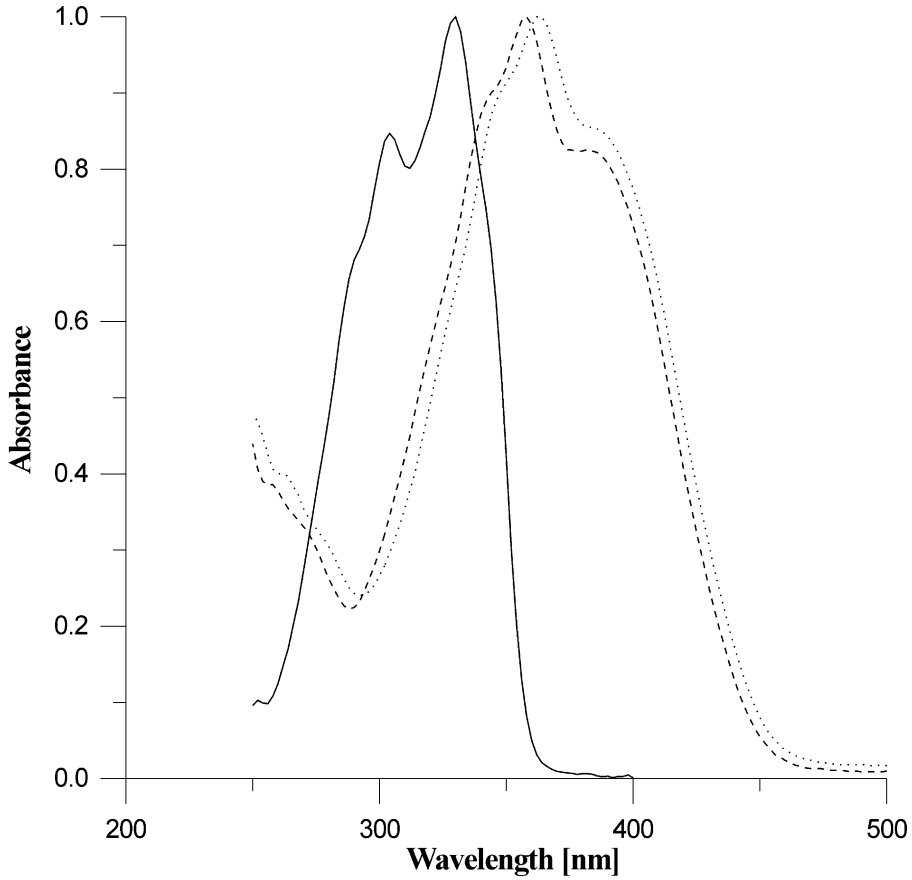


Fig. 1. Absorption spectra of **1** (—), **2a** (– – –) and **2b** (· · · ·) in acetonitrile.

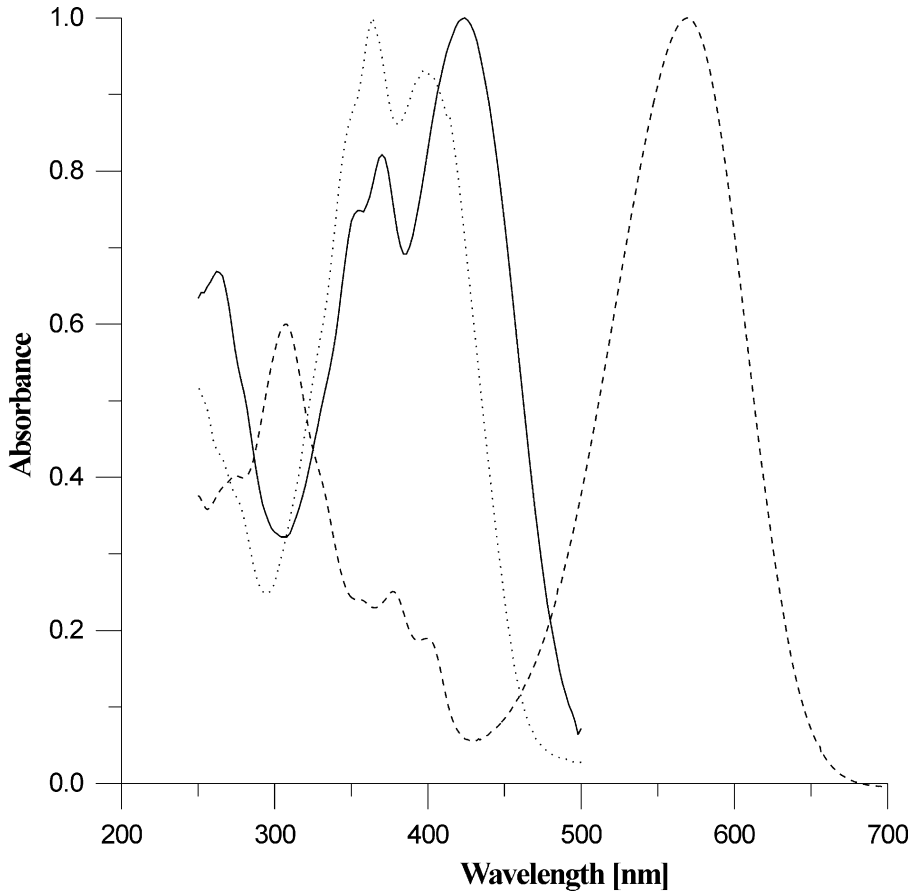


Fig. 2. Absorption spectra of **2c** (· · · ·), **2d** (—) and **2h** (– – –) in acetonitrile.

Table 5
Experimental position of the first absorption band of compounds (**2**) in acetonitrile

Compound	R_1	R_2	λ_{max} (nm)	ε (l/mol.cm)
a	H	H	390	27,000
b	H	Cl	400	23,300
c	H	CH_3	398	25,600
d	H	OCH_3	424	27,300
e	H	C_6H_5	384	27,400
f	H	$N(CH_3)_2$	530	36,100
g	H	$N(C_2H_5)_2$	547	23,000
h	CH_3	$N(C_6H_{13})_2$	569	28,000

(Figs. 4–6). The solvent differs strongly in polarity and the possibility to form the H-bond.

From the presented spectra it is evident, that practically no solvent effect was observed. Only in the case of **2f**, the colour of solution gets deeper by going from dibuthyl ether to acetonitrile. No effect of H-bond was found.

The substances under study exhibit no fluorescence.

3.4. Calculation

The geometry of the molecules in the electronic ground state was calculated using AM1 method (at the "precise" level), the excited state characteristics were calculated using INDO/S-CI and CNDO/S-C methods with modified Nishimoto–Mataga gamma integrals as coded in Win MOPAC version 2.0 package.

The PPP method was used for calculation of electronic transition characteristics in π-approximation

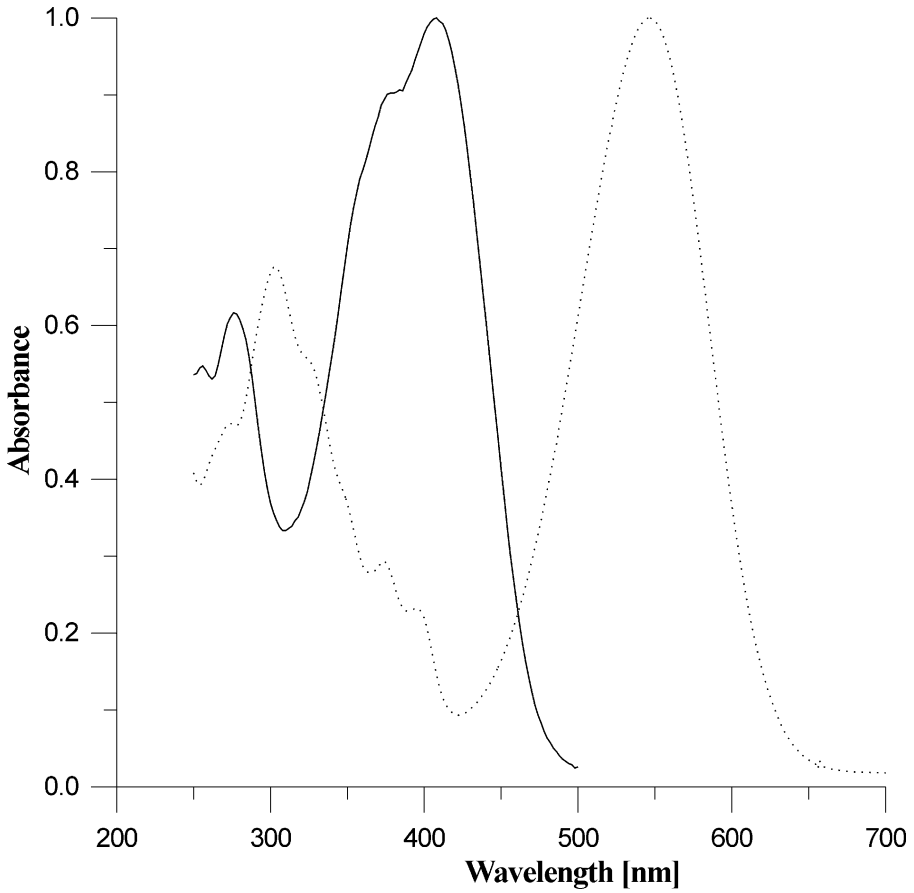


Fig. 3. Absorption spectra of **2e** (—) and **2g** (· · ·) in acetonitrile.

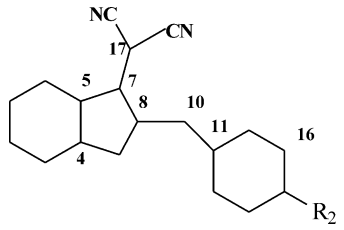
(PISYSTEM 98 for windows package, available from Dr. R. Naef, Im Budler 6, CH-4419, Lupsingen, Switzerland).

The main features of the geometry of the studied systems in the ground state are the bending of the malononitrile group out of the indan-2-ylidene plane and the rotation of the phenyl ring around the bond 10C–11C (Table 6).

It is evident, that a substitution on the phenyl ring does not influence the geometry of the system practically at all. Only the rotation angle around the 10C–11C bond is somewhat changing in the range 33–38° in dependence on the substituent.

From the calculations (Table 7) it is possible to make some conclusions:

Table 6
Numbering convention and selected structural data for the studied molecular system calculated by AM1 method



Torsion angles	R_2 = H	R_2 = –N(CH$_3$)$_2$
4C–5C–7C–17C	165°	165°
17C–7C–8C–10C	27°	27°
8C–10C–11C–16C	−142°	−147°

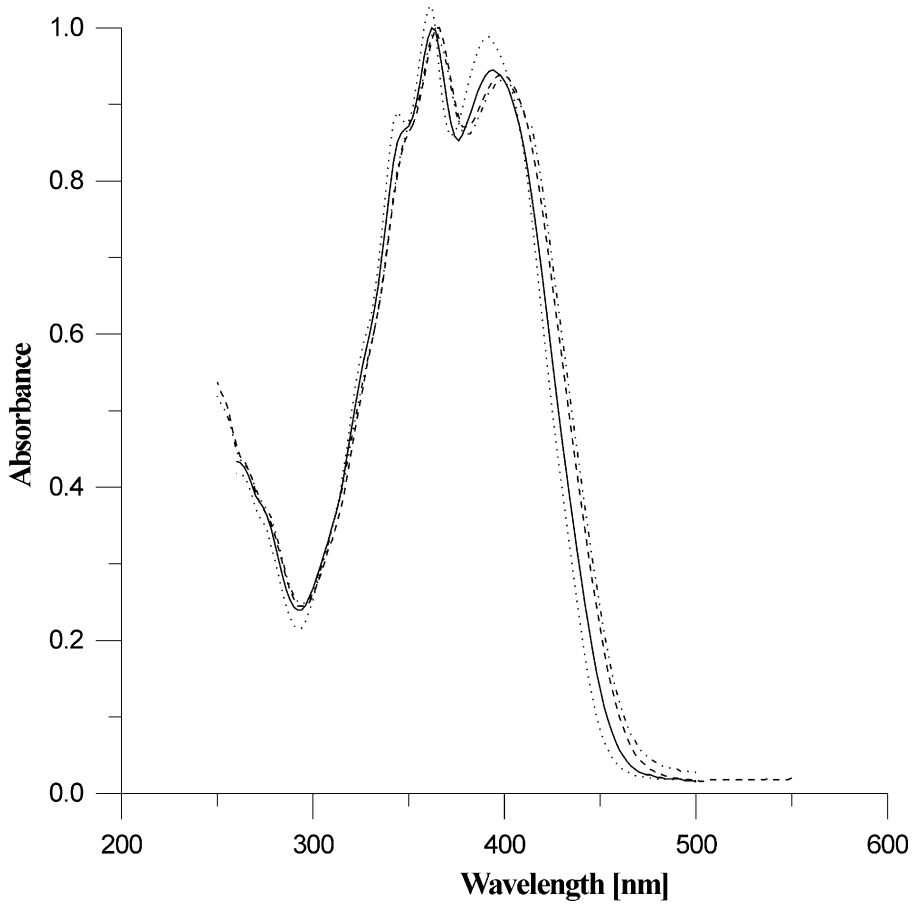


Fig. 4. Absorption spectra of substance **2c** in dibutyl ether (· · · ·), ethyl acetate (—), acetonitrile (– · · –) and methanol (- - - -).

Table 7
Experimental and theoretical transition energies (nm) for the first absorption band of studied compounds

	R_2	1	2	3	4	5
a	H	390	398	435	360	359
b	Cl	401	393	434	–	358
c	CH_3	398	414	437	369	365
d	OCH_3	424	418	440	370	363
f	$N(CH_3)_2$	530	513[a]	541[a]	392	375
g	$N(C_2H_5)_2$	547	544[a]	561[a]	394	376

(1) Experimental values in CH_3CN; (2) PPP, optimized geometry (see text); (3) PPP, full planar geometry; (4) INDO/S, AM1 optimized geometry; (5) CNDO/S, AM1 optimized geometry.

[a] $N(NR_2)$ planar.

- the PPP method for planar geometry, but with phenyl ring distorted around 10C–11C bond by the angle according to AM1 results, predicts the λ_{max} well;
- the PPP method for full planar geometry predicts a more bathochromic absorption band; agreement with experimental results is then better for systems with strong electron donor substituents;
- as could be expected [7] the INDO/S and CNDO/S procedures for AM1 optimised geometry predict more hypsochromic transition energies;
- according to the methods used, the first intensive absorption band of all substances

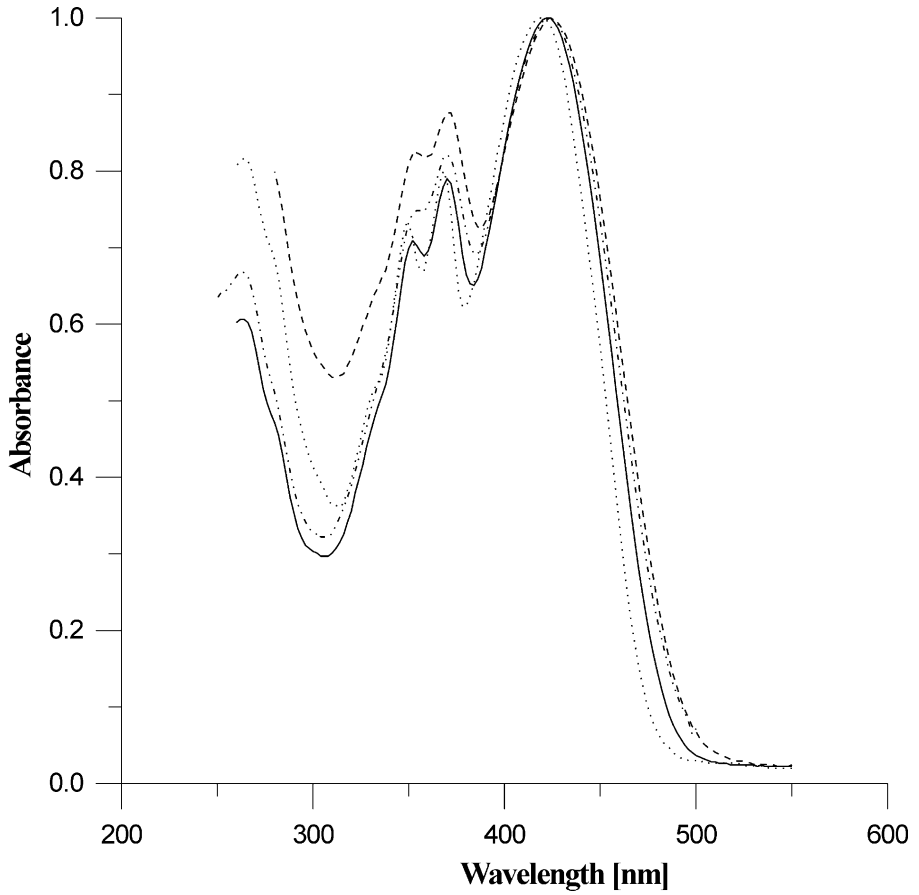


Fig. 5. Absorption spectra of substance **2d** in dibutyl ether (· · · ·), ethyl acetate (—), acetonitrile (– · · –) and methanol (- - - -).

corresponds to the pure HOMO–LUMO π–π* electronic transition (mixing coefficients 0.92–0.96) and the oscillator strengths are high (0.60–0.90).

- by the analysis of the changes of π-electron densities in S_1 state, it was found, that the first band in the spectrum is connected with transfer of electron density from substituted phenyl to the indanylidenemalononitrile skeleton (Fig. 7).

3.5. Coloristic characteristics

Coloristic characteristics of the prepared dyes were also determined from the standpoint of their application as disperse dyes for polyester fibres.

Table 8
Colour fastness to washing on polyester (150 105/C 06)

Dye	Washing 40 °C			Washing 60 °C		
c	4–5	4–5	4–5	4–5	3–4	4–5
d	4–5	4–5	4–5	4–5	4	4–5
f	4–5	4–5	4–5	4–5	4–5	4–5

Table 9
Colour fastness to acid and alkaline perspiration on polyester (150 105/E 04)

Dye	Acid perspiration			Alkaline perspiration			Exhaustion (%)
c	4–5	5	5	4–5	5	5	80
d	4–5	5	5	4–5	5	5	54
f				4–5	4–5	4–5	72, 94[a]

[a] In the presence of alkylbenzensulfonate.

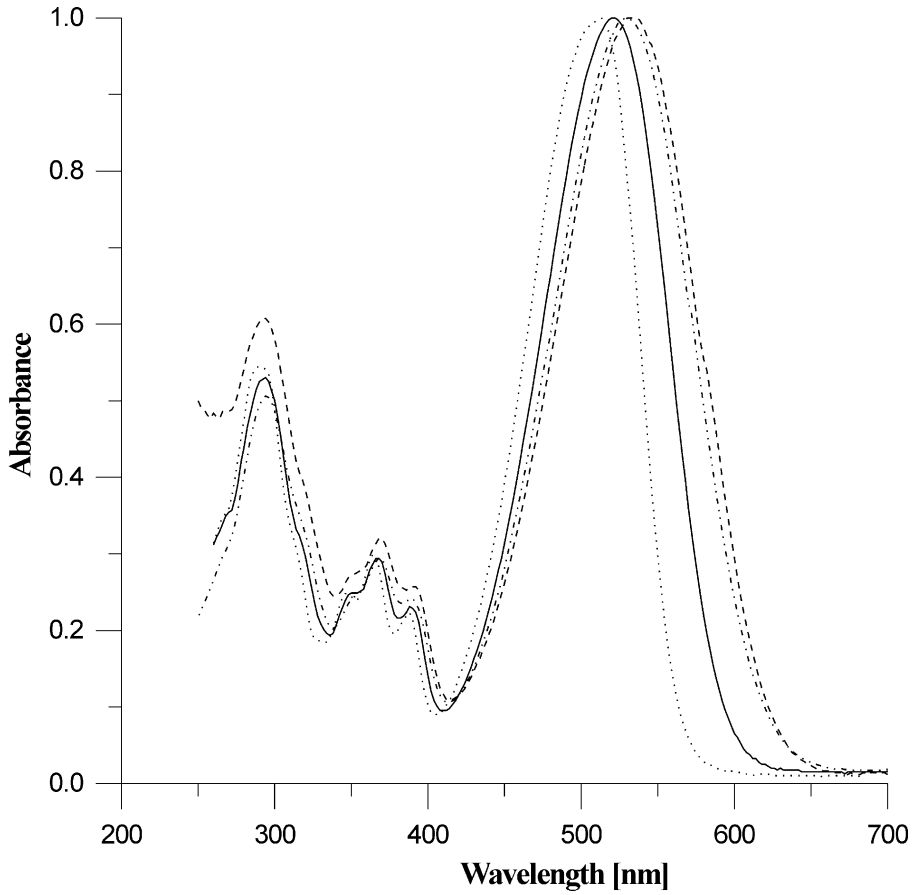


Fig. 6. Absorption spectra of substance **2f** in dibutyl ether (· · · ·), ethyl acetate (—), acetonitrile (– · · –) and methanol (- - - -).

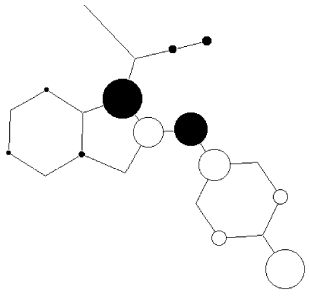


Fig. 7. π-Electron density alteration on S_0–S_1 excitation of dye **2f**.

Table 10
Colour fastness under synthetic light (xenotest) and fixing by dry heat (in sublimation)

Dye	Strength of colouring (%)	Xenotest light	Dry heat	
			180 °C	210 °C
c	1	3	4/1	1/1
d	1	2	4/1	1/1
f	1	1	4–5/1–2	4/1
g	1	1		
h	1	1		

Wet fastness properties of **2c**, **2d** and **2f**, were examined. The prepared dyes show good wet fastness, as it is usual with disperse dyes (Tables 8 and 9).

The test of stability in sublimation was performed for dyes **2c**, **2d** and **2f**. From Table 10 it is perceptible that testing dyes have relatively to low

sublimation and light fastness for their practical application.

4. Conclusion

The aim of this research was to find a new type of methinic disperse dyes. It was found that 1-indanylidenemalononitrile can be condensed with different aromatic aldehydes resulting in formation the series of new dyes. By this procedure the dyes of yellow, orange and violet shades were prepared.

The constitution of new compounds was confirmed by the elemental analysis and NMR spectra. The UV/vis spectra in different solvents were measured. Very good accordance between theoretical PPP transition energies and experimental spectra for the first absorption band of compounds was found.

Colouristic characteristics of the dyes were also determined for their applications as disperse dyes for textile industry. Unfortunately, the dyes show very poor light fastness.

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