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Synthesis and spectra of tetrakis (4-dimethylaminophenyl) hexadienes

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Abstract

Condensation of 1,1-*bis*(4-dimethylaminophenyl)ethylene with substituted hydroxyketones in acetic anhydride in the presence of perchloric acid yielded NIR polymethine dyes. The VIS–NIR spectra of the dyes were measured and interpreted by the semi-empirical AM1 method of quantum chemistry. The influence of the molecular structure variations and electron density distribution on the position of the peaks with the largest wavelengths has been studied. The results indicate that increase of the polyene rigidity and planarity might lead to the increase of maximum absorption wavelength. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymethine dyes; Synthesis; VIS–NIR spectra; Quantum chemistry calculations; Structure variations; Electronic structure

1. Introduction

A number of polymethine dyes absorbing in the NIR region have been synthesised recently [1]. Among them, the dyes with several aryl substituents containing electron donors in the ortho or para position are of considerable importance [2–4]. In our previous paper [5] the synthesis of a series of 1,1,5-*tris*-(4-dimethylaminophenyl)-3-R-divinylene carbenium perchlorate dyes has been reported. The VIS–NIR absorption spectra of these dyes were measured and interpreted theoretically using a semi-empirical quantum-chemistry treatment. The dependence of the position of absorption maximum, $\lambda_{\max}$ on R substituents and the total charges of their cations, and simple models of the solvent effect were studied. A systematic shift of $\lambda_{\max}$ to higher wavelengths with an increase of positive charge could be used to mimic some solvent effects (such as polarisation due to the solvent permittivity) in real systems. On the contrary, protonation removes the chromophore planarity and brings about a decrease of (max value in accordance with experimental data. The structure of the dyes has been described using the simple statistical characteristics, i.e. arithmetic mean values and root mean square deviations σ of bond distances, atomic charges and bond indices over the carbon skeleton of individual chromophores. The similarity of these characteristics for the individual chromophores in the dyes might be more important than planarity factors, as demonstrated by the mutual interplane angles of the pentadiene chain and the phenyl rings. The results of quantum chemistry calculations indicate that an additional (dimethylamino) phenyl bonded to the C_5

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atom might lead to an increase of λ_{max} and the use of substituents with higher electron donor or acceptor characteristics should not significantly affect the position of λ_{max}.

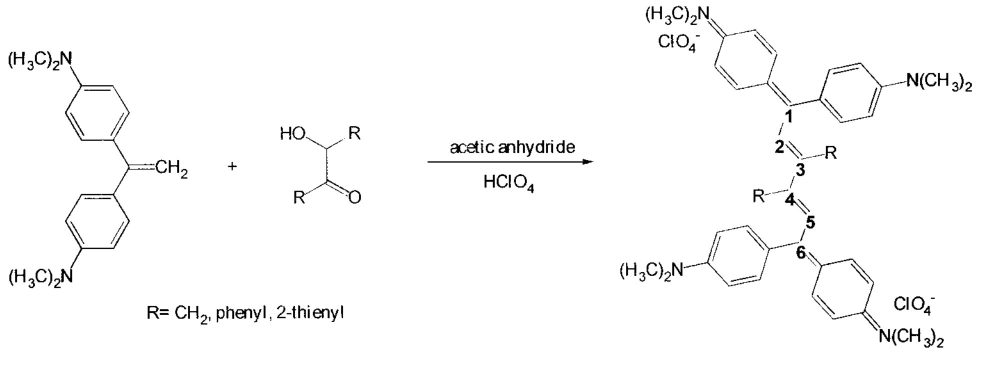
This paper reports the synthesis of a series of simple 1,1,6,6-tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadiene 1,6-dicarbenium diperchlorates. Dyes with similar structure are of particular interest in the optical data storage field because they exhibit a very intense absorption band at about 800 nm. The VIS–NIR absorption spectra of the synthesised dyes have been measured and then interpreted on the basis of mutual chromophores interaction and its relationship to the geometry and electron structure (its variations have been modelled by various total charges of the molecule). For comparison, simpler compounds such as 1,1-*bis*(4-dimethylaminophenyl)ethylene have also been studied in the same way.

2. Results and discussion

The preparation of tetraaryl polymethine dyes by condensing 1,1-*bis*(4-dimethylaminophenyl) ethylene with substituted hydroxyketones in acetic anhydride in the presence of perchloric acid is shown in Scheme 1.

The hydroxyketones, benzoin and tenoin were prepared by benzoin condensation of appropriate aldehydes in dry ethanol and in the presence of 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride as a catalyst. 1,1-*bis*(4-dimethylaminophenyl)ethylene used was obtained from Michler's ketone by Grignard reaction with methylmagnesium iodide in diethylether. The dyes B–D were prepared by the reaction of diketones with 1,1-*bis*(4-dimethylaminophenyl)ethylene. Selected experimental characteristics of the dyes under study are presented in Table 1 (with the atoms numbered as in Scheme 1). The most intense λ_{max} values and calculated maximum wavelengths, λ_m, of the visible electron spectra of the systems are presented in Table 2. The A1h geometry is derived from the A0 system by bonding of a single proton H^+ to the C_2 atom. Analogously, the B3h systems were derived from the B2 system by bonding H^+ to the N atom. A1′, A2′ and A1h′ systems correspond to alternative geometries obtained accidentally (not by optimisation starting from the less charged systems). In Tables 3 and 4, the rings bonded to C_1 are presented before the C_6 bonded ones. In Table 5, the data presented in parentheses correspond to extended hexadiene chains including additional chain-to-(dimethylamino)phenyl bonds.

Analogously to our previous paper [5], the calculated λ_{max} values for the B2, C2 and D2 systems exhibit systematic shifts towards shorter wavelengths compared to the experimental data (Tables 1 and 2). This is explainable by the neglect of all external interactions in the isolated model systems. Larger wavelengths can be obtained by the dye molecule (ion) charge variation modelled by the additional H^+ bonding, but the intensity of the maximal wavelength λ_m decreases (Table 2). The



Scheme 1.

Table 1
Selected experimental characteristics of the dyes

Dye	Compound	M.W.	yield (%)	λ_{max} (nm)
A	1,1-*bis*-(4-dimethylaminophenyl)ethylene	266.385	60	–
	1,1,6,6-Tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadien-1,6-dicarbenium diperchlorates			
B	R = −methyl	785.746	60	627, 805
C	R = −phenyl	907.887	60	595, 642, 802
D	R = −2-thienyl	919.932	55	597, 628, 803

Table 2
The most intense wavelengths λ_{max} and maximal λ_m values in the VIS-NIR spectra of the systems (oscillator strength values are in parentheses)

Compound	System	Charge	λ_{max} (nm)	λ_m (nm)
1,1-*bis*-(4-dimethylaminophenyl)ethylene	A0	0	340(0.3), 219(0.5)	341(0.1)
	A1	1	560(0.3)	560(0.3)
	A1′[a]	1	609(0.2)	609(0.2)
	A2	2	906(1.0)	906(1.0)
	A2′[b]	2	928(1.2)	928(1.2)
A0 + H^+ (bonded to C_2 atom)	A1h	1	666(1.8)	666(1.8)
	A1h′[c]	1	531(1.1)	531(1.1)
1,1,6,6-tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadienium cations				
R = −methyl	B1	1	619(0.5), 555(0.4) 435(0.8), 399(0.4)	619(0.5)
	B2	2	511(1.1), 510(1.2) 382(1.0)	511(1.1)
	B3[d]	3	715(0.2), 678(0.1) 604(0.1)	736(0.1)
	B4	4	858(1.7), 494(1.7) 484(1.9)	858(1.7)
B2 + H^+ (bonded to N atom)	B3h	3	532(1.3), 420(1.1) 330(0.3)	532(1.3)
R = −phenyl	C2	2	492(2.6), 369(0.8) 250(0.4)	510(0.1)
	C3	3	610(0.1), 471(0.1) 402(0.1), 398(0.1)	610(0.1)
R = −2-thienyl	D2	2	505(1.0), 500(1.5) 349(1.1), 273(0.9)	505(1.0)
	D3	3	640(0.3), 598(0.3) 456(0.3), 447(0.4)	680(0.2)

[a] ca 11 kcal/mol more stable than A1 geometry.
[b] ca 46 kcal/mol more stable than A2 geometry.
[c] Practically the same stability as A1h geometry.
[d] Negative values occur due to different ground state for configuration interaction.

protonation does not have such a destructive effect on λ_{max} as in 1,1,5-*tris*-(4-dimethylaminophenyl)-3-R-divinylene carbenium perchlorates. However, a simple positive charge increase of the compound under study has stronger effects. Further trends are analogous to those reported previously [5]. The bond lengths increase with the positive charge of the dye for all chromophores, but this may not

Table 3
Deviations from planarity in the studied systems

System	(C–C–C)$_{\mathrm{phen}}$–N	(C–C)$_{\mathrm{phen}}$–N-C$_{\mathrm{met}}$	(C–C–C)$_{\mathrm{chain}}$–C$_{\mathrm{phen}}$	(C–C)$_{\mathrm{chain}}$–(C–C)$_{\mathrm{phen}}$	(C–C–C–C)$_{\mathrm{chain}}$
A0	4,4	18,19	–	37,38	–
A1	0,1	2,1	–	32,32	–
A1$'$	0,4	0,13	–	20,44	–
A2	0,0	1,1	–	32,32	–
A2$'$	2,1	1,1	–	97,21	–
A1h	0,1	1,1	–	31,18	–
A1h$'$	0,0	1,0	–	24,26	–
B1	4,5,0,0	16,17,1,1	40,23,27,40	29,40,26,26	11,11,4
B2	1,1,1,1	1,1,1,1	58,61,56,59	21,24,22,25	2,31,2
B3	1,0,1,0	2,1,1,1	57,60,60,64	26,19,23,20	3,28,3
B4	1,2,1,2	1,1,1,1	61,65,62,66	15,28,15,28	4,30,4
B3h	0,1,1,1	63,0,1,1	63,56,66,69	61,56,20,24	2,31,2
C2	1,1,1,1	1,1,2,1	65,69,65,69	23,22,23,22	1,27,1
C3	1,1,0,1	1,1,1,1	64,69,64,69	23,22,23,22	1,27,1
D2	1,1,1,1	2,1,1,1	68,71,67,71	20,24,20,24	0,38,0
D3	1,1,1,1	2,0,1,1	66,69,66,71	21,24,18,26	1,37,1

hold for their standard deviations and for inter-chromophore bonds (Tables 4 and 5). A reverse trend holds for bond order values. The mean atomic charges indicate a relatively uniform distribution of the additional charges among individual chromophores. Small changes of λ_{max} with variation in R substituents (Tables 1–4) can be explained by small changes in the electronic structure of (dimethylamino)phenyl chromophores, and substituents with higher electron donor or acceptor character may not lead to significant λ_{max} increase.

Mutual angles of individual chromophore planes depend also on the system charge (Table 3). In contrast to 1,1,5-tris-(4-dimethylaminophenyl)-3-R- divinylene carbenium perchlorates [5] which have planar pentadiene chains, in 1,1,6,6-tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadien-1,6- dicarbenium diperchlorates the crucial factor is the non-planarity of the hexadiene chains. This may be responsible for the lower calculated λ_{max} value and, for the case of the solvent effect, for the worse agreement with experimental data than in [5]. Consequently, additional rings implemented into the hexadiene chain should give rise to higher rigidity and higher planarity, leading to higher λ_{max}. Compounds of this type will be reported in a future paper.

3. Experimental

3.1. General

VIS/NIR spectra were recorded using a diode array fibre optic spectrometer Ocean Optics S1000.

Acetoin, benzaldehyde, 2-thiophenecarbaldehyde, 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride and Michler's ketone were supplied by Aldrich. All chemicals were of reagent grade and were used without further purification unless otherwise specified.

The hydroxyketones, benzoin and 2-thenoin were synthesised by published methods [6].

*3.2. Preparation of 1,1-*bis*(4-dimethylaminophenyl) ethylene [7]*

A suspension of methylmagnesium iodide (prepared from 7.29 g of Mg and 18.58 ml CH_3I) in 75 ml of diethyl ether under argon was treated with 19.2 g of Michler's ketone, m.p. 173–176°C, dissolved in 225 ml of hot benzene. After heating under reflux for 6 h, the mixture was chilled and treated with saturated ammonium chloride solution. The crude product was fractionally crystallised from ethanol to give

Table 4
Statistical characteristics of benzene rings in the studied systems

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
A0	1.402	0.011	−0.093	0.091	1.383	0.044
	1.402	0.011	−0.093	0.090	1.384	0.444
A1	1.408	0.025	−0.072	0.111	1.344	0.140
	1.408	0.025	−0.072	0.111	1.344	0.140
A1′	1.415	0.031	−0.054	0.089	1.298	0.188
	1.405	0.015	−0.094	0.097	1.347	0.073
A2	1.415	0.038	−0.055	0.110	1.314	0.245
	1.415	0.038	−0.059	0.111	1.314	0.245
A2′	1.413	0.024	−0.060	0.058	1.300	0.122
	1.414	0.026	−0.055	0.067	1.292	0.148
A1h	1.409	0.026	−0.084	0.163	1.334	0.164
	1.410	0.029	−0.081	0.168	1.328	0.186
A1h′	1.410	0.027	−0.083	0.166	1.331	0.174
	1.410	0.027	−0.082	0.166	1.330	0.176
B1	1.408	0.015	−0.092	0.080	1.325	0.078
	1.407	0.014	−0.094	0.081	1.331	0.069
	1.408	0.025	−0.084	0.160	1.337	0.154
	1.408	0.024	−0.085	0.159	1.338	0.149
B2	1.411	0.030	−0.079	0.166	1.324	0.198
	1.410	0.028	−0.083	0.163	1.330	0.177
	1.411	0.030	−0.079	0.166	1.325	0.197
	1.410	0.028	−0.083	0.163	1.330	0.177
B3	1.414	0.034	−0.066	0.125	1.318	0.219
	1.416	0.037	−0.067	0.135	1.314	0.238
	1.416	0.035	−0.066	0.134	1.314	0.237
	1.414	0.034	−0.068	0.130	1.319	0.219
B4	1.420	0.045	−0.049	0.109	1.302	0.301
	1.417	0.038	−0.052	0.094	1.312	0.240
	1.420	0.046	−0.049	0.109	1.302	0.302
	1.416	0.038	−0.052	0.094	1.312	0.240
B3h	1.401	0.005	−0.087	0.017	1.396	0.024
	1.420	0.047	−0.059	0.148	1.300	0.315
	1.413	0.033	−0.077	0.164	1.320	0.217
	1.410	0.029	−0.083	0.162	1.328	0.186
C2	1.411	0.029	−0.081	0.165	1.328	0.184
	1.410	0.028	−0.079	0.164	1.328	0.182
	1.410	0.028	−0.081	0.165	1.338	0.179
	1.410	0.029	−0.079	0.164	1.328	0.182
C3	1.417	0.029	−0.080	0.164	1.325	0.193
	1.416	0.029	−0.079	0.163	1.325	0.190
	1.411	0.030	−0.058	0.069	1.282	0.174
	1.411	0.030	−0.056	0.070	1.283	0.171
D2	1.411	0.030	−0.078	0.167	1.324	0.197
	1.410	0.027	−0.085	0.167	1.331	0.173
	1.411	0.030	−0.078	0.167	1.324	0.197
	1.410	0.027	−0.081	0.163	1.331	0.173
D3	1.411	0.030	−0.081	0.159	1.326	0.196
	1.412	0.031	−0.076	0.157	1.321	0.213
	1.415	0.038	−0.065	0.091	1.290	0.220
	1.410	0.029	−0.093	0.114	1.327	0.158

Table 5
Statistical characteristics of the aliphatic chains in the studied systems (values in parentheses correspond to extended chains including chain-to-phenyl bonds)

System	Interatomic distances		Atomic charges		Bond indices	
	Mean (10^{-10} m)	σ (10^{-10} m)	Mean	σ	Mean	σ
A0	1.343	–	−0.116	0.104	1.878	–
	(1.424)	(0.058)			(1.292)	(0.414)
A1	1.367	–	−0.052	0.028	1.676	–
	(1.420)	(0.037)			(1.270)	(0.287)
A1′	1.375	–	−0.083	0.068	1.529	–
	(1.423)	(0.035)			(1.225)	(0.219)
A2	1.383	–	−0.084	0.032	1.497	–
	(1.416)	(0.023)			(1.264)	(0.165)
A2′	1.357	–	−0.102	0.006	1.721	–
	(1.425)	(0.049)			(1.253)	(0.333)
A1h	1.482	–	−0.006	0.240	1.016	–
	(1.438)	(0.031)			(1.181)	(0.119)
A1h′	1.482	–	−0.006	0.240	1.017	–
	(1.439)	(0.031)			(1.181)	(0.116)
B1	1.413	0.022	−0.020	0.151	1.280	0.129
	(1.423)	(0.022)			(1.215)	(0.128)
B2	1.419	0.058	+0.010	0.179	1.337	0.396
	(1.417)	(0.043)			(1.309)	(0.298)
B3	1.421	0.058	−0.013	0.147	1.335	0.399
	(1.417)	(0.044)			(1.319)	(0.298)
B4	1.422	0.060	+0.092	0.362	1.334	0.406
	(1.418)	(0.046)			(1.330)	(0.312)
B3h	1.420	0.057	−0.008	0.154	1.335	0.395
	(1.419)	(0.049)			(1.319)	(0.331)
C2	1.421	0.058	+0.030	0.177	1.334	0.401
	(1.418)	(0.043)			(1.306)	(0.300)
C3	1.422	0.053	−0.008	0.134	1.273	0.313
	(1.421)	(0.040)			(1.254)	(0.236)
D2	1.422	0.061	+0.041	0.172	1.336	0.416
	(1.418)	(0.045)			(1.309)	(0.312)
D3	1.425	0.062	−0.005	0.109	1.293	0.374
	(1.419)	(0.047)			(1.282)	(0.281)

7.5 g (60%) of 1,1-*bis* (4-dimethylaminophenyl) ethylene, m.p. = 122–124°C. The material balance indicates that a by-product is also obtained, viz. 2,2-bis-(4-dimethylaminophenyl)-propane, m.p. = 60–75°C.

3.3. 1,1,6,6-Tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadien-1,6-dicarbenium diperchlorates

A mixture of 2.66 g (0.01 mol) of 1,1-*bis*(4-dimethylaminophenyl)ethylene, mp = 122–124°C, (0.005 mol) of hydroxyketone and 10 ml of acetic anhydride was treated with a solution of 0.68 g (0.005 mol) of 71% perchloric acid in 10 ml of acetic anhydride. The blue mixture was heated on the steam-bath for 70 min with occasional swirling. After cooling, the mixture was treated with ether and product isolated by filtration.

4. Quantum-chemical calculations

The standard semiempirical AM1 method of quantum chemistry (AMPAC program package)

[8,9] was used to find the optimal geometries of 1,1-*bis*(4-dimethylaminophenyl)ethylene and 1,1,6,6-tetrakis-(4-dimethylaminophenyl)-3,4-R,R-2,4-hexadienium dications (R = methyl, phenyl or 2-thienyl) with various charges (see Table 1). All calculations were performed in higher precision (keyword PRECISE) using the Davidon–Fletcher–Powell optimisation procedure [10,11]. The electronic structure characteristics were evaluated in terms of charges of individual atoms and bond indices of individual bonds [12]. The electron spectra lines of the systems under study were calculated using the single excited configuration interaction method with 163 (singlet states) or 162 configurations (doublet states) [13]. Analogously to our previous paper on *tris*-(4-dimethylaminophenyl) divinylenes [5] the systems under study are described by arithmetic mean values and root mean square deviations (σ) of the bond distances, atomic charges and bond indices over the carbon skeleton of individual chromophores. The perturbations of the planar π-bond framework are described by the deviations from planarity (dihedral angles).

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