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Dyes and Pigments 53 (2002) 119–128

DYES and PIGMENTS

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Electric field induced second harmonic generation (EFISH) measurements on absorbing compounds: push–pull substituted anilines

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Received 5 November 2001; received in revised form 23 November 2001; accepted 5 December 2001

Abstract

This paper deals with the influence of various electron acceptors, which contain at least two cyano groups (obtained from reactions with malononitrile, tetracyanoethene, tetracyanoquinodimethane, dimeric malononitrile), on the generation of second harmonic light of donor–acceptor-substituted anilines. For EFISH measurements, which were performed on solutions in 1,4-dioxane and acetone a Yag–Nd laser was used. The influence of the solvent on the SHG efficiency is discussed shortly and compared to solvatochromic effects. The measurement data were corrected for absorptive effects so that absorbing compounds can be compared to non-absorbing ones. Increasing the acceptor strength not only bathochromically shifted the longest wavelength UV–vis absorption band but also leaded to an enhancement of $\mu\beta$-values obtained by the EFISH measurements. Trends of hyperpolarizabilities calculated by semi-empirical molecular orbital methods by and large conformed those found experimentally. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: EFISH; Swivel cell; AM1; ZINDO

1. Introduction

Materials with nonlinear optical (NLO) properties are of great interest for the development of photonic devices like electro-optic modulators, frequency generators, and all optical switches [1,2]. Organic dyes, with an electron donating and an electron-accepting group at opposite ends of a conjugated π-system, are leading candidates as NLO materials. The stronger the electronic effect of donors and acceptors, the lower is the energy difference between HOMO and LUMO, the higher is the maximum absorption wavelength and, by and large, the higher is the polarizability of the compound. One could expect that a high linear polarizability should bring along high hyperpolarizabilities as well. It turned out, however, that a high linear polarizability was necessary but not always sufficient to obtain large hyperpolarizabilities [3,4]. Thus, concepts, which can explain the influence of different substituents on the maximum absorption wavelength of dyes [5], cannot be applied directly, if optical nonlinearity is discussed. Polarizabilities

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PII: S0143-7208(01)00103-6

of polymethines were investigated thoroughly and a unified description was suggested [6]. It was shown that the structures (aromatic, aromatic-quinoide) of the substituents as well as bond length alternation in the polymethine chain were of crucial importance for the nonlinear optical response of the compounds [3,4,6–8].

Structure–property relationships have remained of great interest since the development of NLO materials has started 25 years ago [9,10]. Practical as well as theoretical considerations are based on series of similar compounds, which are measured or calculated, respectively. If it comes to a quick experimental screening, EFISH measurements are used to determine second order polarizabilities. They allow estimating the second harmonic generation (SHG) in terms of $\mu\beta$, where μ means the dipole moment of the molecule and β is the second order polarizability (this is the nonlinearity responsible for mixing two input waves at frequencies ω_1 and ω_2 to produce an output wave at frequency $\omega_3 = \omega_1 + \omega_2$).

Cyano acceptor groups have been used in dye chemistry for years. Since the notable optical nonlinearity of some cyano compounds was reported about 15 years ago [11], some work has been reported on this issue [12–19]. As a complement to the experimental determination of hyperpolarizabilities, computational methods have become increasingly important [20]. Consequently, results (dipole moments and $\mu\beta$-values) obtained with the aid of semi-empirical (AM1 [21,22] and ZINDO [23,24]) molecular orbital calculations on some of the compounds investigated or simplified models thereof, will also be presented.

From the practical point of view the development of new materials also means to find easily accessible (and polymerizable) compounds, which can be produced at a reasonable price. This is why we haven chosen cyano substituted and *N,N*-disubstituted (mainly dialkylated) anilines for this study.

2. Results and discussion

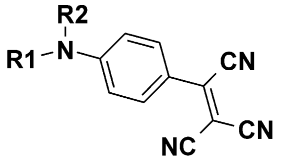
The syntheses of the compounds in this paper were rather straightforward. So tricyanovinyl compounds **1a–f** were obtained in high yields by combining the anilines with tetracyanoethene (TCNE) in dimethylformamide or acetonitrile [25–28]. **2a,b** were prepared from the nitroso compounds and malononitrile (MDN). Condensation reactions of nitroso-anilines and formyl anilines with dimeric MDN gave **3a–c** and **4a–c** respectively, while **5a** was obtained from *N*-ethyl-*N*-hydroxyethyl-aniline and tetracyanoquinodimethane (TCNQ) [29,30]. (See Scheme 1 for compounds **1a–i** and **2a–d** and Scheme 2 for **3a–c**, **4a–c** and **5a,b**.)

Polymerizable dyes **1g and h**, **2c and d**, and **5b** were synthesized from the corresponding hydroxy compounds and excess methacryloyl chloride. Reactions in boiling acetonitrile gave up to 95% yields, if molecular sieves were used to trap the hydrochloric acid evolving during the reactions. The use of tertiary amines or alkali hydroxides gave products of poor quality and low yields [28,31]. Amino compound **1a** was converted to **1i** using the same procedure.

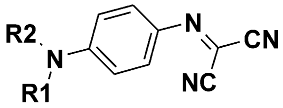
All EFISH measurements reported in this paper were performed with the swivel cell setup [32]. The laser we have used was a YAG–Nd laser with an emission wavelength of 1064 nm. This meant, that only compounds **1i** and **4a–c** did not show any notable absorption at the SHG wavelength of 532 nm. **1a** and **1g,h**, **2a–d**, and **5a and b** had very low or low absorption coefficients at 532 nm ($300 \leqslant \varepsilon \leqslant 12{,}000$). **1b–f** and **3a–c** showed high absorption coefficients (for vis data of selected compounds see Table 1).

As a rule the amplitude of the signal decreases and the Maker fringes [33] become less pronounced, if the extinction coefficient increases and it had been discussed earlier that in EFISH experiments absorption phenomena had to be regarded [9,34–37]. The method we have recently published [32] includes molar extinction coefficients in the calculation of the EFISH data. We could also show that—as the refractive index of a medium changes noticeably near its maximum absorption—the precise determination of dispersion ($\Delta n = n_{1064\mathrm{nm}} - n_{532\mathrm{nm}}$) was crucial for an accurate evaluation of the measurement data and had to be taken into account.

The $\mu\beta$ values of compounds **1a–g** were between 980 and $1400 \cdot 10^{-68}$ $\mathrm{Cm^5/V}$ in 1,4-dioxane.



1	R^1	R^2
a	H	methyl
b	methyl	methyl
c	methyl	n-butyl
d	methyl	n-octyl
e	ethyl	2-hydroxyethyl
f	2-hydroxyethyl	2-hyroxyethyl
g	ethyl	2-(methacryloyloxy)ethyl
h	2-(methacryloyloxy)ethyl	2-(methacryloyloxy)ethyl
i	methyl	methacryloyl

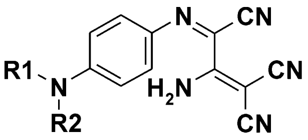


2	R^1	R^2
a	methyl	methyl
b	ethyl	ethyl
c	ethyl	2-(methacryloyloxy)ethyl
d	2-(methacryloyloxy)ethyl	2-(methacryloyloxy)ethyl

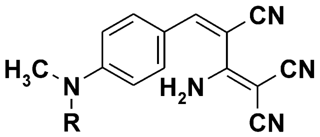
Scheme 1. Compounds **1a–i** and **2a–d**.

Measurements in acetone yielded $\mu\beta$ values of $1584 \cdot 10^{-68}$ Cm^5/V for **1b**, $1282 \cdot 10^{-68}$ Cm^5/V for **1e** and $1373 \cdot 10^{-68}$ Cm^5/V for **1h** (for EFISH data and dipole moments see Table 2). Compound **1i** is different from other compounds **1**. It contains two electron withdrawing groups (a methacryloyl group on the anilino nitrogen in addition to the tricyanovinyl group) instead of a donor and an acceptor like other compounds **1**. So it was no surprise that **1i** had a very low $\mu\beta$ ($71 \pm 10 \cdot 10^{-68}$ Cm^5/V in 1,4-dioxane).

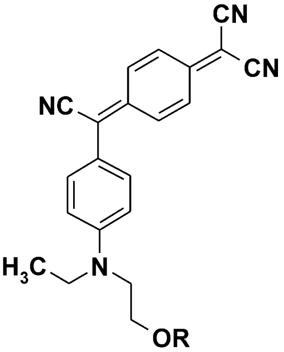
The hydroxyl groups in **1e**, **1f** and **5a** were transformed into methacryloyloxy groups to give polymerizable compounds **1g**, **1h** and **5b**, respectively. While attachment of the electron acceptors increased the dipole moments ($\mu_{calc.}$) of **1e** and **1f** by approx. 5 and 40%, respectively, the SHG-intensity in 1,4-dioxane was reduced by 10–20%. A comparable



3	R^1	R^2
a	methyl	n-hexyl
b	methyl	1-methylpropyl
c	ethyl	2-hydroxyethyl



4	R
a	n-butyl
b	n-hexyl
c	n-octyl



5	R
a	H
b	methacryloyl

Scheme 2. Compounds **3a**–**c**, **4a**–**c** and **5a** and **b**.

Table 1
Vis data of selected compounds

No.	$\varepsilon_{532\ \mathrm{nm}}$ (dioxane)	$\varepsilon_{532\ \mathrm{nm}}$ (acetone)	$\lambda_{\max}$ (nm) (dioxane)	$\lambda_{\max}$ (nm) (acetone)	$\Delta\lambda_{\max}$ (nm)
1b	14,800	76,850	497	513	16
1e	21,500	37,940	503	516	13
1h	6850	26,910	488	503	15
1i	110	<100	395	397	2
2a	4400	7190	474	488	14
2b	6170	15,300	480	490	10
2d	2780	7180	468	480	12
3a	34,590	n.e.[a]	513	524	11
3b	38,900	52,100	515	525	10
3c	36,900	47,470	514	526	12
4a	<100	150	427	433	6
4b	<100	170	434	434	0
4c	300	240	n.e.[a,b]	437	n.e.[a]
5a	11,700	3780	650	700	50
5b	7800	3060	632	676	44

[a] Not estimated.

[b] Two overlapping maxima.

effect was observed in case of compounds **5a,b**. While $\mu_{\mathrm{calc.}}$ of **5b** was 20% higher than $\mu_{\mathrm{calc.}}$ of **5a** and SHG was 14% lower in 1,4-dioxane, SHG in acetone went down by more than 40%.

Comparison of tricyanovinyl compounds **1a**–**h** with dicyanomethyleneamino compounds **2a**–**d** showed differences of approx. 15–25 nm between compounds **2** and **1** (depending on the solvent) of the maximum absorption wavelengths. The differences in long wave absorptions coincided with differences in SHG efficiencies ($\mu\beta$ in 1,4-dioxane between 980 and $1403\cdot10^{-68}$ $\mathrm{Cm^5/V}$ for **1a**–**h** versus 650 and $1120\cdot10^{-68}$ $\mathrm{Cm^5/V}$ for **2a**–**d**). The imino nitrogen in **2** instead of the cyanomethylene group in **1** resulted in somewhat lower values for of $\mu_{\mathrm{calc.}}$. The differences of $\lambda_{\max}$ (**1b** versus **2a** or **1h** versus **2d**) were 20 and 23 nm in 1,4–dioxane and 23 and 25 nm in acetone. The influence of an imino nitrogen can also be seen when comparing derivatives **3a**–**c** with **4a**–**c**, which were obtained from dimeric malononitrile (DMDN) and *p*-nitroso-anilines and *p*-amino-benzaldehydes, resp. Calculated dipole moments showed differences of approx. 2 Debye, the difference of $\lambda_{\max}$ was about 80 nm in 1,4-dioxane and 90 nm in acetone. $\mu\beta$ values of **4a**–**c** ($109–155\cdot10^{-68}$ $\mathrm{Cm^5/V}$ in 1,4-dioxane and $137–150\cdot10^{-68}$ $\mathrm{Cm^5/V}$ in acetone) were very small compared to the ones we have

Table 2
Experimental (in 1,4-dioxane and acetone) and calculated $\mu\beta$-values (AM1-PECI, in diethyl ether and acetone) and calculated dipole moments ($\mu_{\text{calc.}}$) of **1a–i**, **2a–d**, **3a–c**, **4a–c**, and **5a** and **b**

Compound	$\mu_{\text{calc.}}$ (Debye) (ether)	$\mu\beta$ EFISH (10^{-68} Cm^5/V) (1,4-dioxane)	$\mu\beta$ AM1-PECI (10^{-68} Cm^5/V) (ether)	$\mu_{\text{calc.}}$ (Debye) (acetone)	$\mu\beta$ EFISH (10^{-68} Cm^5/V) (acetone)	μ AM1-PECI (10^{-68} Cm^5/V) (acetone)
1a	6.81	978±199	97	6.45		98
1b	7.16	1190±151	123	6.83	1584±229	124
1c	7.12	1403±217	117	6.80		116
1d	7.04	1380±140	111	6.79		110
1e	6.25	1267±100	98	5.91	1282±92	98
1f	6.91	1264±70	116	6.66		116
1g	9.16	1047±172	132	8.90		132
1h	6.50	1153±175	72	6.25	1373±84	72
1i	7.62	71±10	71	7.44		71
2a	7.23	650±77	122	6.72	789±131	121
2b	6.22	1117±229	90	5.89	874±70	89
2c	6.65	1004±83	105	6.34		105
2d	9.12	673±42	114	9.28	850±54	121
3a	9.27	1404±62	110	9.00		110
3b	9.66	1381±85	136	9.22	1301±85	135
3c	10.08	1225±76	120	9.65	1222±124	119
4a	7.08	109±36	103	6.83		102
4b	7.03	168±41	99	6.79	137±9	99
4c	6.99	155±55	98	4.32	150±7	98
5a	7.66	2056±121	515	7.33	1305±229	518
5b	8.99	1810±123	399	8.70	715±63	399

obtained for **3a–c** (1225–1404·10^{-68} Cm^5/V in 1,4-dioxane and 1222–1301·10^{-68} m^5/V in acetone).

5a Contained a tricyanoquinodimethenyl group as electron acceptor and was obtained from TCNQ and *N*-ethyl-*N*-hydroxyethyl-aniline using a modified procedure from literature [29,30]. TCNQ is well known to be an extremely strong electron acceptor [38,39] and has already been used in NLO materials (for some typical examples see [40]). According to theoretical considerations the aromatic-quinoide ground state of **5a,b** should add to SHG intensity noticeably [3]. Thus it was no surprise that the $\mu\beta$s of **5a** and **5b** (2056·10^{-68} Cm^5/V and 1810·10^{-68} Cm^5/V in 1,4-dioxane) were more than 1.5 times the $\mu\beta$ values of the corresponding tricyanovinyl substituted anilines [$\mu\beta$(**1e**) = 1267·10^{-68} Cm^5/V, $\mu\beta$(**1g**) = 1047·10^{-68} Cm^5/V]. The change was mainly due to higher values of β. The changes of dipole moments ($\mu_{\text{calc.}}$) were less pronounced (+20% for **1e** versus **5a** and −2% for **1g** versus **5b**).

2.1. The influence of solvent polarities on the EFISH data

In principle, all solvents can be used for EFISH experiments in the swivel cell. In practice it is easier to use non-polar ones because of the lower signal of the solvent itself and the use of polar solvents is limited to solutes with high SHG [32]. There were hints that SHG efficiency might depend on the polarity of the solvent [41–43]. This is why we have performed EFISH experiments in acetone as well as in 1,4-dioxane.

2.2. Solvatochromic effects and SHG efficiency

Attempts have been made to obtain β from solvatochromic methods and compare them to data, which were obtained from classical EFISH experiments [34]. Correlations between maximum absorption wavenumber and $\mu\beta$ obtained from EFISH experiments in 1,4-dioxane and acetone are given in Figs. 1 and 2. Nearly all anilines discussed in this paper showed higher long wave absorptions in acetone compared to 1,4-dioxane (see also Table 1). The solvatochromic effect was low (or zero) in case of yellow compounds **1i** and **4a**–**c** and typically between 10 and 20 nm for compounds **1a**–**h**, **2a**–**c**, and **3a**–**c**. Solvatochromic effects were large for compounds **5a**,**b**. The maximum absorption wavelength of **5a** was shifted from 650 nm in 1,4-dioxane to 700 nm in acetone. A similar shift (44 nm) was found for **5b**. Solvatochromic effects gave no clear hints concerning the SHG intensity. In 1,4-dioxane as solvent experimental $\mu\beta$-values increased with the strength of the acceptor (as indicated by its influence on the wavelength of the absorption maxima; see Table 1 and Fig. 1). In acetone a comparable relationship was discernible, if only compounds **1**–**4** were regarded. **5a**,**b**, which were structurally rather dissimilar from **1** to **4** obviously were different (Fig. 2).

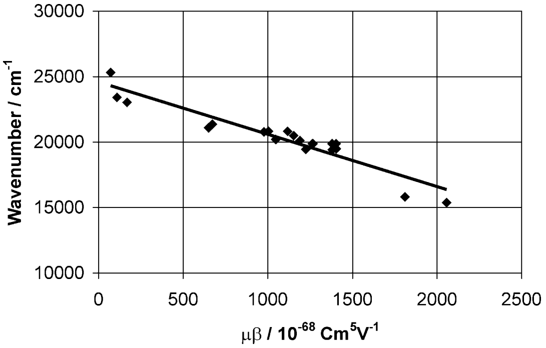


Fig. 1. Wavenumbers of absorption maxima versus $\mu\beta$ (10^{-68} Cm^5/V) of compounds **1a**–**i**, **2a**–**d**, **3a**–**c**, **4a**–**c**, and **5a** and **b** (experimental data, in 1,4-dioxane).

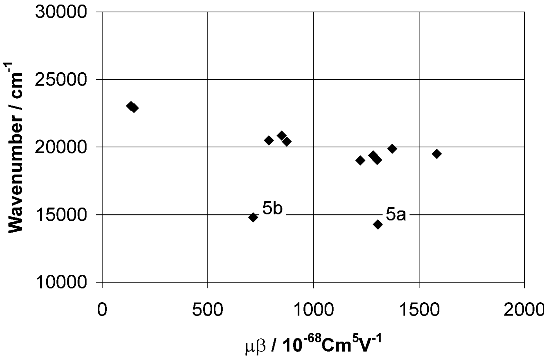


Fig. 2. Wavenumbers of absorption maxima versus $\mu\beta$ (10^{-68} Cm^5/V) of selected compounds (experimental data, in acetone).

It is well known that increasing the donor and/or the acceptor strength need not necessarily result in higher optical nonlinearity but rather there exists—for a given parent chromophor—an optimal donor–acceptor combination [3,44,45]. The present results seem to indicate that this optimal combination also depends on the solvent used for the EFISH measurement.

2.3. Calculated hyperpolarizabilities

Proper treatment of solvent effects substantially influences calculated $\mu\beta$-values [46]. Recently we have shown that inclusion of quadrupole contributions to the solvent model significantly improves the agreement between experimental UV/vis spectra and those calculated by the ZINDO procedure [47]. Thus, $\mu\beta$-values were calculated by ZINDO with inclusion of solvation (1,4-dioxane; acetone) by the SCRF model [46] taking into account the quadrupole effects. The computational procedure used for the calculation of molecular hyperpolarizabilities is based on the SOS approach [48]. Within the framework of this perturbational treatment the individual components β_{ijk} of the hyperpolarizability tensor are inversely proportional to the difference $\Delta E = (\Delta E_{\text{exc.}} - 2\cdot E_{\text{laser}})$ between the calculated electronic transition energy $\Delta E_{\text{exc.}}$ and twice the excitation energy of the laser used ($E_{\text{laser}} = 1.17$ eV in the present case). Consequently, for compounds where $\Delta E_{\text{exc.}} \approx 2\cdot E_{\text{laser}}$ the perturbational treatment no longer is valid. Obviously, this is the case for compounds **5**, especially in acetone. Apart from this model structure, generally the calculations grossly underestimated $\mu\beta$-values. This might partly be due to an overestimation of $\Delta E_{\text{exc.}}$ (the mean error between experimental values for the longest wavelength absorption band and calculated transition energies is 1100 (acetone) and 1600 (dioxane) cm^{-1}, respectively. Increasing the solvent polarity slightly enhanced the calculated $\mu\beta$-values. In reasonable agreement with experimental data in 1,4-dioxane, calculated $\mu\beta$-

Table 3
Comparison of calculated $\mu\beta$-values (10^{-68} Cm^5/V) for selected compounds (gas phase and different solvents)

No.	$\mu\beta$/Gas AM1-PECI	$\mu\beta$/Ether AM1-PECI	$\mu\beta$/Dioxane ZINDO	$\mu\beta$/Acetone AM1-PECI	$\mu\beta$/Acetone ZINDO
1b	105	123	116	124	122
1i	73	71	55	71	58
2a	106	122	128	121	135
3a	99	110	355	110	377
4a	70	103	90	102	96
5a	451	515	3262	518	5425

values increased in the order **4** ($96{\cdot}10^{-68}$ Cm^5/V) < **1** ($116{\cdot}10^{-68}$ Cm^5/V) ≈ **2**($128{\cdot}10^{-68}$ Cm^5/V) < **3** ($355{\cdot}10^{-68}$ Cm^5/V) < **5** ($3262{\cdot}10^{-68}$ Cm^5/V). As found also experimentally, acylation of the amino group to give **1i** results in the lowest calculated hyperpolarizability ($55{\cdot}10^{-68}$ Cm^5/V).

It has been shown that hyperpolarizabilities obtained by the AM1/CISD method might be superior to those from ZINDO calculations [49,50]. Excitation energies obtained by such an AM1 single and double perturbational CI-treatment (10 electrons, 10 orbitals) are considerably higher than those obtained by the ZINDO procedure (up to 10,000 cm^{-1}). Thus, the problem in the calculation of hyperpolarizabilities arising from $\Delta E_{\text{exc.}} \approx 2{\cdot}E_{\text{laser}}$ is of no concern here for compounds **5a** and **b**. Besides these model compounds, results obtained thereby are quite similar to ZINDO $\mu\beta$-values (see Table 3).

3. Conclusions

In 1,4-dioxane as the solvent all anilines discussed in this paper showed a good correlation of $\mu\beta$ and μ with the maximum absorption wavelength. In acetone a less clear-cut relationship between $\mu\beta$ and $\lambda_{\max}$ can bee seen, especially in case of tricyanoquinodimethanes **5a** and **b**. Several of the investigated compounds showed substantial absorption in the region of the SHG wavelength. Thus, a meaningful comparison of these substances with those transparent in this special region required the application of a model, which allows for correction of the absorption.

It seems that in the cases of simple molecules like *p*-acceptor-substituted *N,N*-alkylated anilines there is—at least in solvents of low polarity—a direct correlation between acceptor strength, long wave absorption and first hyperpolarizability β. So the introduction of a tricyanoquinodimethenyl group into the aniline resulted in a distinct bathochromic shift and optimum SHG efficiency. This held true also for anilines with polymerizable side chains. Trends of calculated $\mu\beta$-values show reasonable agreement with experimental findings. In contrast absolute values are off by up to an order of magnitude.

4. Experimental

4.1. General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra, Perkin-Elmer Spectrophotometer 298 (KBr pellets), ^{1}H NMR and ^{13}C NMR spectra, Bruker 369 AM (all NMR spectra are referenced to tetramethylsilane), UV/vis spectra, Hitachi U-3501.

EFISH measurements were performed in the swivel cell, which we have described earlier [32]. All EFISH-experiments were performed in triplicate on solvents and solutions, with the fillings of the cell replaced after each measurement. Concentration series were used to ensure reliable results. Pure solvents and solutions of *p*-nitro-aniline (*p*NA) were measured prior to the samples and all results referenced on *p*NA in 1,4-dioxane ($\mu\beta = 18.3{\cdot}10^{-68}$ Cm^5 V^{-1}; see [51], Appendix 2).

The anilines used as starting materials were obtained from commercial suppliers and distilled immediately before use. The aldehydes (precursors of **4a**–**c**) and nitroso compounds (for compounds **2a**–**d** and **3a**–**c**) were prepared using standard procedures [52]. The synthesis of dimeric malononitrile used for compounds **3a**–**c** and **4a**–**c** was performed according to Ref. [53]. The following compounds were prepared according to procedures from literature: **1a**–**h** [25–28], **2a** and **b** [54], **2c** and **d** [28], **3a**–**c** [17], **4a**–**c** [17].

4.2. Syntheses

*4.2.1. 4-[Cyano-(4-dicyanomethylen-cylohexa-2,5-dienyl)-methyl]-N-ethyl-N-(2-hydroxyethyl)-aniline (**5a**) [12]*

N-Ethyl-*N*-(2-hydroxyethyl)-aniline (10 mmol) and TCNQ (10 mmol) were reacted in boiling acetonitrile (100 ml) for 2 h. Subsequently the reaction mixture was radiated by means of a Hg-lamp for 4 h. The product was the filtered by suction and the filtrate refluxed and radiated again for 2 and 4 h, respectively. After filtration of the product the procedure was repeated a third time. The combined products were dried and recrystallized from acetonitrile.

Yield 83%, dark green crystals m.p.: 214 °C (acetonitrile). IR: $\nu = 3600–3300$, 2220 (CN), 1615, 1580, 1520 $\mathrm{cm^{-1}}$. ^{1}H NMR: $\delta = 1.18$ (*t*, 3H, $-CH_2-\underline{CH}_3$), 3.40–3.60 (m, 4H, $-N-CH_2-$), 4.96 (*t*, $-\underline{CH}_2-OH$), 7.04–7.79 (*m*, 8H, aromatic protons and protons of the cyclohexadiene ring) ppm (the proton of the hydroxy group is not visible). UV/vis (acetone) $\lambda_{\max.}$ (log ε): 700 (4.748) nm; (1,4-dioxane) $\lambda_{\max.}$ (log ε): 649 (4.963) nm. Calculated for $C_{21}H_{18}N_4O$: C, 73.8; H, 5.3; N, 16.4; found: C, 73.4; H, 5.2; N, 16.4.

*4.2.2. Synthesis of polymerizable compounds **1i**, **5b***

General procedure, adopted from [28]: **1a** or **5a** (20 mmol) and finely ground mol sieves 4 Å (4 g) were stirred in acetonitrile (40 ml). Methacryloyl chloride (25 mmol) was added and the mixture heated under reflux (reaction times given below). The reaction mixtures were filtered by suction while still hot and the mol sieves washed with hot acetonitrile. Solvent and excess methacryloyl chloride were removed under reduced pressure and the solid residues recrystallized and dried on air.

*4.2.2.1. 4-Tricyanovinyl-N-methyl-N-methacryloyl-aniline (**1i**).* Twenty hours; yield 72%, orange-red crystals m.p.: 122 °C (chloroform/ether). IR: $\nu = 2980$, 2240, 2220, 1650, 1625, 1595, 1570, 1535, 1510 $\mathrm{cm^{-1}}$. ^{1}H NMR: $\delta = 1.93$ (*s*, 3H, $C-CH_3$), 3.47 (*s*, 3H,$-N-CH_3$), 5.05 (*s*, 2H, $=CH_2$), 7.38 (*d*, 2H, aromatic protons), 8.06 (*d*, 2H, aromatic protons) ppm. UV/vis (1,4-dioxane) $\lambda_{\max.}$ (log ε): 397 (4.218) nm. Calculated for $C_{16}H_{12}N_4O$: C, 69.6; H, 4.4; N, 20.3; found: C, 69.2; H, 4.3; N, 20.2.

*4.2.2.2. 4-[Cyano-(4-dicyanomethylen-cylohexa-2,5-dienyl)-methyl]-N-ethyl-N-(2-methacryloyloxyethyl)-aniline (**5b**).* Forty-eight hours; yield 90%, dark blue crystals m.p.: 134 °C (acetonitrile/water). IR: $\nu = 3000–2800$, 2220 (CN), 1725, 1615, 1585, 1520 $\mathrm{cm^{-1}}$. ^{1}H NMR: $\delta = 1.28$ (*t*, 3H, $-CH_2-\underline{CH}_3$), 1.95 (*s*, 3H,$-CO-\underline{CH}_3$), 3.58 (*q*, $-N-\underline{CH}_2-CH_3$), 3.76 (*t*, $-N-CH_2-\underline{CH}_2-$), 4.36 (*t*, $-CH_2-\underline{CH}_2-O-$), 5.61–6.10 (*d*, 2H, $=CH_2$), [6.86 (*d*), 7.20–7.40 (*m*), 7.45–7.75 (*m*) aromatic protons and protons of the cyclohexadiene ring] ppm. UV/vis (1,4-dioxane) $\lambda_{\max.}$ (log ε): 632 (4.596) nm; (acetone) $\lambda_{\max.}$ (log ε): 676 (4.472) nm. Calculated for $C_{25}H_{22}N_4O_2$: C, 73.2; H, 5.4; N, 13.7; found: C, 73.0; H, 5.4; N, 12.9.

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