FULL PAPER

Influence of Methyl Substituents in Phenylenediamine Derivatives on the Properties of Electrophotographic Layers

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Abstract. Substituent effects on the electrophotographic properties of N,N,N',N'-tetraarylphenylenediamines **1a–i** derivatives have been investigated to obtain a molecular design guide to enhance photosensitivity of hole transporting materials for organic photoreceptors. The introduction of methyl groups into N-substituted phenyl moiety in all the cases increases considerably the photosensitivity and reduces the residual potential, moreover, the m- and p-substitution was found to be the most promising. On the other hand, the presence of alkyl substituents enhances the stability of glassy state of such low molecular weight organic compounds.
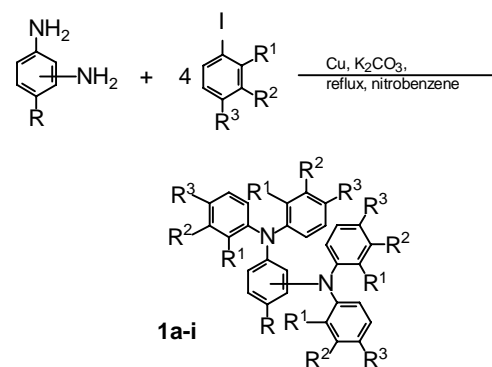
Electrophotographic systems with photosensitive layers containing film-forming polymeric substances (polycarbonate, polyamide or polyester resins) together with low-molecular-weight charge transporting materials are widely used in the imaging industry [1]. Replacement of photoconductive polymers (polyvinylcarbazole, polyepoxypropylcarbazole) [1] by low-molecular-weight substances expanded greatly the assortment of the compounds, suitable for the named purpose. Recently, a variety of transporting materials, involving hydrazone, stilbene, pyrazoline, imine, carbazole or triarylamine moiety have been generated [2–7]. They ensure rapid charge transporting ability, high photosensitivity and durability of the layers. Meanwhile, numerous investigations are being carried out aiming to enhance their hole drift mobility, however until now only few concrete recommendations have been made with regard to the molecular structure modification. Only limited data are available, concerning the influence of the presence and location of alkyl substituents on the qualitative parameters of electrophotographic layers (EPL). The importance of these groups in N,N,N',N'-tetraarylbenzidine derivatives while constructing the frame of an effective photoconductor has been demonstrated [8].

The aim of this work was the investigation of the influence of methyl groups and their location on the quality of EPL in N,N,N',N'-tetraarylphenylenediamine derivatives as they belong to the class of triarylamines, which have been recently mentioned among the most effective charge transporting materials in various electro-optical applications [9–14]. Methyl groups were selected because of the commercial availability of the starting materials, moreover there is a very slight difference between methyl and ethyl groups in this case [8].

Results and Discussion

N,N,N',N'-tetraarylphenylenediamines **1a–i** were synthesized by the Ullmann reaction [15] of 1,2-, 1,3-, 1,4-phenylenediamines and 2,4-toluenediamine with cor-

Product	Phenylenediamine	R	R¹	R²	R³
a	o-	H	H	H	CH₃
b	m-	H	H	H	H
c	p-	H	H	H	H
d	m-	H	CH₃	H	H
e	m-	H	H	CH₃	H
f	m-	H	H	H	CH₃
g	m-	H	H	CH₃	CH₃
h	m-	CH₃	H	H	CH₃
i	m-	CH₃	H	CH₃	CH₃

Scheme 1 Synthesis of N,N,N',N'-tetraarylphenylenediamines **1a–i** by the Ullmann reaction

responding iodoarenes in nitrobenzene at reflux in the presence of catalyst – copper powder and anhydrous potassium carbonate (the latter combines with the liberating hydrogen iodide).

The selection of solely 1,3-phenylenediamine derivatives for further investigations was made after coating EPL of 1,2-bis(4,4'-dimethyldiphenylamino)benzene (**1a**), 1,3- and 1,4-bisdiphenylaminobenzene (**1b,c**) which had been obtained from 1,2-, 1,3- and 1,4-phenylenediamines. We have found, that only **1b** was of good compatibility with polymeric binder material, thus giving high quality EPL.

By interaction of 1,3-phenylenediamine with 2-, 3-, 4-methyliodobenzenes following hole transporting materials, possessing *o-*, *m-*, *p*-substituents, were synthesized: 1,3-bis(2,2'-dimethyldiphenylamino)benzene (**1d**), 1,3-bis(3,3'-dimethyldiphenylamino)benzene (**1e**), and 1,3-bis(4,4'-dimethyldiphenylamino)benzene (**1f**). From the obtained compounds and charge generating materials (fluorenone-based bisazopigment (λ_{max} = 620 nm) [16] and phthalocyanine dye (λ_{max} = 830 nm)) double-layered xerographic photoreceptors were made, and their electrophotographic parameters, i.e. photosensitivity (*S*) and residual potential (U_R), were measured. These are shown in the table 1.

Table 1 Electrophotographic parameters of electrophotographic layers (EPL) of *N,N,N',N'*-tetraarylphenylenediamine derivatives **1a**–**i**

Com- pound	$\lambda = 620$ nm		$\lambda = 830$ nm	
	S, m^2/J	U_R, %	*S*, m^2/J	U_R, %
1a	–	–	–	–
1b	46.0	31.0	88.6	34.1
1c	–	–	–	–
1d	69.6	12.8	101.4	16.6
1e	97.2	7.7	142.0	5.1
1f	107.0	6.2	132	6.3
1g	110.2	5.9	144.0	4.0
1h	107.0	6.2	145.9	4.6
1i	120.5	5.6	153.1	2.9

From the data presented in the table it can be stated that the methyl substituents at *o*-position enhance the photosensitivity 1.51 and 1.14 times (**1d** and **1b** are compared), at the same time reduce the residual potential 2.42 and 2.05 times; while the same substituents at *m*-position increase of photosensitivity 2.11 and 1.60 times and decrease of U_R 4.02 and 6.69 times is observed (**1e** and **1b**); *p*-substitution (**1f** and **1b**) enhances the photosensitivity 2.32 and 1.50 times and reduces the residual potential 5.0 and 5.41 times. Thus, substitution by methyl groups in all the cases increases the photosensitivity considerably and reduces the residual potential (the lower U_R is favourable). As can be seen from the table 1 these properties have been improved and the most

desirable are in the case of *m-* and *p*-substitution. This can be explained by σ-π conjugation and a consequent electron density delocalization, as it is reported [8], that one of the main conditions for improving electrophotographic parameters is electron density delocalization of hole transporting material HOMO orbital. Inhibition of delocalization caused by steric hindrance of methyl groups at the *o*-position gives the reduced effect comparing to *m-* and *p*-substitution.

With the aim of evaluating the influence of the two introduced alkyl groups on the electrophotographic properties 1,3-bis(3,3',4,4'-tetramethyldiphenylamino)benzene (**1g**) was synthesized. As expected, the *p-* and *m*-substitution of phenyl ring by methyl groups enhanced the photosensitivity and, at the same time reduced the residual potential (**1f** and **1g**). Measurement of electrophotographic layers, that had been obtained on the basis of 1,3-bis(4,4'-dimethyldiphenylamino)-4-methylbenzene (**1h**) and 1,3-bis(3,3',4,4'-tetramethyldiphenylamino)-4-methylbenzene (**1i**), led to the conclusion that the presence of an alkyl group in the linking fragment – 1,3-phenylenediamine ring – has no significant influence, though some improvement of electrophotographic properties is observed. The other conclusion was confirmed again – the presence of two methyl groups is superior to that of a single one.

Since the major properties of EPL directly depend on the amount of the transporting material doped in the polymeric binder, and the optimum results are usually achieved if EPL contains 40–60% of transporting material [8], in this paper we'll describe an important property of such low-molecular weight organic compounds – the ability to form stable glasses. With the aim of detailed investigation of the crystallization ability of *N,N,N',N'*-tetraarylphenylenediamines, differential scanning calorimetry (DSC) analysis was performed.

The results were obtained by comparison of 1,2-, 1,3- and 1,4-phenylenediamines *N,N,N',N'*-tetraarylated derivatives **1a**–**c**. Compound **1c**, that melts at 195 °C (DSC) differs from the others for its highest crystallization ability. Repeated heating gives an endothermic peak at the same place. From this can be concluded, that the 1,4-phenylenediamine derivative undergoes an easy and rapid crystallization, forming a very unstable amorphous phase if any. This is in agreement with Wirth's postulate [17] that points molecular symmetry to be a predominant factor with respect to the inclination to form glasses. Interesting results were obtained while performing DSC analysis of **1a** (Fig.1a). On the first heating quite usual melting is observed. On the second run an intensive crystallization occurs with a maximum at 109 °C. In this process a metastable crystalline phase forms which tends to undergo transition into a stable one (repeated scanning at a 5 °C/min rate gives two peaks, corresponding to two eutectic melting points).

From the thermogram it is seen that the first crystalline phase is the predominant one, but the ratio tends to change during time.

By thermal scanning of 1,3-bisdiphenylaminobenzene (**1b**) curves, similar to that of the compound **1a**, are obtained (Fig. 1b), however this substance seems to form a more stable amorphous state. On the second and third heating 1,3-phenylenediamine derivative **1a** only slightly crystallizes thus forming little of metastable crystalline phase. Thus, 1,2- and 1,3-phenylenediamine derivatives are distinguished by polymorphism. This could be explained by the existence of molecular conformers that make the glassy state more stable, especially for **1b**. Moreover, the corresponding phase transitions in 1,3-phenylenediamine derivative take place at lower temperatures than 1,2- and 1,4-phenylenediamine *N,N,N',N'*-tetraaryl derivatives. As was mentioned earlier, namely due to these properties of 1,3-phenylenediamine derivatives EPL of good film homogeneity can be obtained.

The presence of methyl groups at *o*-position (compound **1d**) enhances the stability of the glassy state in comparison with that of the compound without methyl groups; in this case only slight crystallization is observed after 24 h (Fig. 1c). The best stability of glassy state was exhibited by charge transporting materials **1e–i**, which did not undergo crystallization after the first melt.

DSC analysis curves of 1,3-bis(4,4'-dimethyldiphenylamino)benzene (**1f**) are presented in figure 1d as typical for such a case. Thus, the formation of glassy state is greatly influenced by methyl substituents. Obviously, the introduction of the methyl group at the *o-*, *m-* or *p*-position in *N,N,N',N'*-tetraarylphenylenediamines increases the number of conformers, thus changing the way of packing of the molecules thereby preventing crystallization.

From the DSC analysis data, presented above, following conclusions should be made: *m*-phenylenediamine derivatives are more plastic than *o-*, *p*-derivatives; the presence of methyl substituents enhances the stability of the amorphous state. This illustrates earlier statement that electrophotographic properties can be improved radically by introducing seemingly insignificant alkyl groups. This is an important factor while modeling the structure of organic photoconductors with optimum properties.

Experimental

The UV spectra were recorded on a "Specord UV VIS" in 1,2-dichloroethane, the IR spectra on a "Specord M 80" in KBr pellets. The ^{1}H NMR spectra were determined in deuteriochloroform (CDCl$_3$) on a TESLA BS-487 C (80 MHz) spectrometer, the chemical shifts are expressed in parts per
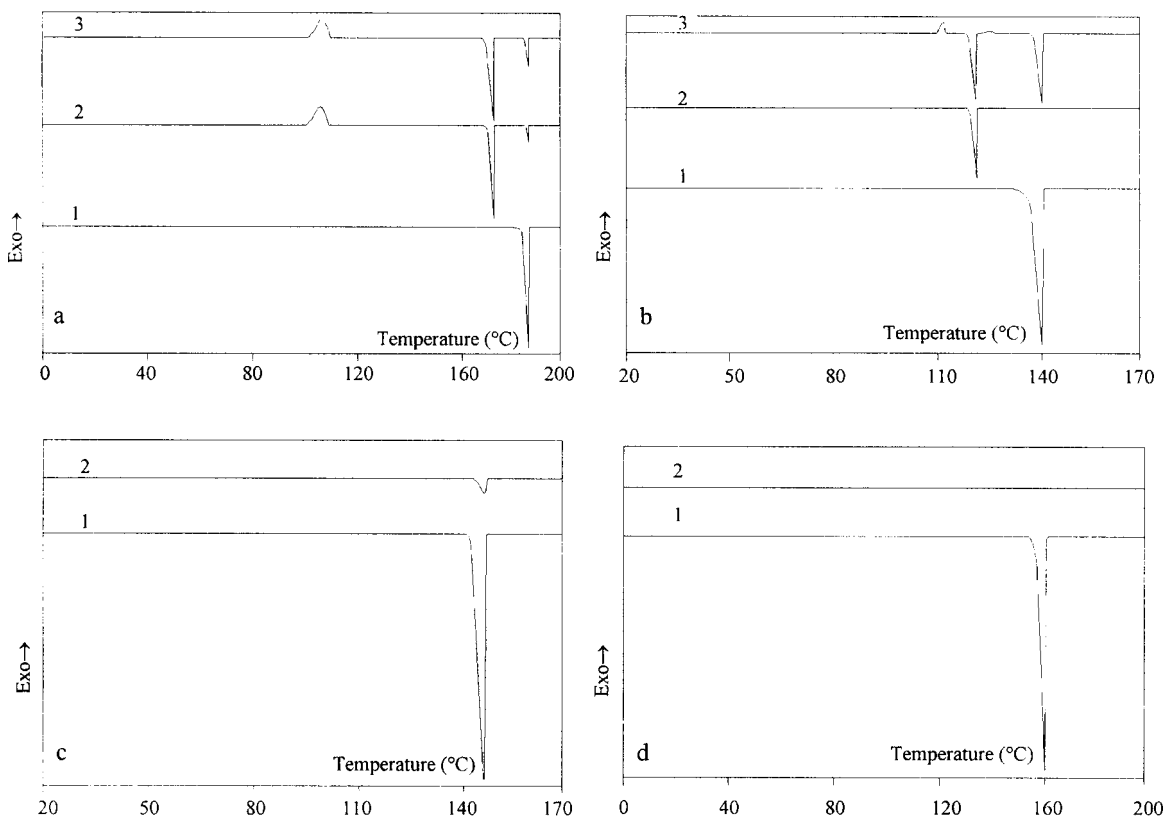

Fig. 1 DSC thermograms of *N,N,N',N'*-tetraarylphenylenediamines (a) **1a**, (b) **1b**, (c) **1d** and (d) **1f**; (1) first heating, (2) second heating, (3) third heating (heating rate 5 °C/min).

million downfield to hexamethyldisiloxane (HMDS) used as internal standard. Differential scanning calorimetry (DSC) analysis was performed (Perkin Elmer DSC-2) at a scan rate 5 °C/min. After the first heating the samples were left to cool to room temperature and were heated again under the same conditions. The third run after 24 h was performed for **1a** and **1b** compounds. The course of reaction and purity of products was controlled by thin-layer chromatography (acetone–n-hexane, 1:4) on plates "Silufol UV-254". Column chromatography was carried out on aluminium oxide (Brockmann II, neutral).

Synthesis of *N,N,N',N'*-Tetraarylphenylenediamines 1a–i (General Procedure)

A 0.5 l flask equipped with a reflux condenser (0.25 m length), attached to a Liebig condenser was charged with diamine (0.02 mol), corresponding iodoarene (0,2 mol), anhydrous potassium carbonate (0.12 mol), and electrolytic copper powder (4 g) in 100 ml of nitrobenzene. The mixture is stirred vigorously under nitrogen at the boiling temperature of nitrobenzene. The reaction mixture is heated at such a rate that water, liberating in the course of the reaction together with a little amount of nitrobenzene and iodoarene is slowly distilled. The distillate is dried over anhydrous magnesium sulphate and returned back into reaction flask. After termination of the reaction (8 h) the copper and inorganic salts are removed by filtration of the hot reaction mixture. Nitrobenzene and unreacted iodoarene is distilled off, and the residue is dissolved in chloroform and then is adsorbed by 100 g of powdered Al_2O_3. The latter is dried and subjected to extraction with n-hexane in a 0.5 l Soxhlet extractor. (The procedure is carried out until hexane turns colourless.). The extraction solution is worked up with activated charcoal and the solvent evaporated. The residue is dissolved in acetone (1:1) and cooled to 0 °C. The separated crystalline products **1a–i** are filtered off. Compounds **1a, 1c, 1e–i** are purified by column chromatography (Al_2O_3, hexane:dichloroethane, 5:1) and subsequent recrystallization from glacial acetic acid or n-octane. Compounds **1b** and **1d** are twice recrystallized from glacial acetic acid and n-octane.

For **1a** yield 33,0%, *m.p.* 139–140,5 °C (acetic acid), [18] *m.p.* 137.5–138 °C.

For **1b** yield 17%, *m.p.* 182–183.5 °C (acetic acid).

For **1c** yield 41,0%, *m.p.* 195.5–196.5 °C (acetic acid), [19] *m.p.* 199–200 °C.

Table 2 Spectral and elemental analysis data of *N,N,N',N'*-tetraarylphenylenediamine derivatives **1a–i**

Compound	IR selected bands ν/cm^{-1}	^{1}H NMR δ/ppm	UV λ_{max}/nm (lg ε)	Molecular Formula (Mol. mass)	Calcd. Found	C C	H H	N N
1a	3030 (=C-H); 2915 (CH$_3$); 818, 760, 720, 710 (=C-H of 1,2- and 1,4-disubstituted benzenes).	2.20 s (12H, 4CH$_3$); 6.50–7.70 m (20H, CH$_{arom.}$).	224 (4.31) 299.8(4.57)	C$_{34}$H$_{32}$N$_2$ (468.64)		87.14 86.89	6.88 6.81	5.98 6.15
1b	3050, 3020 (=C-H); 750, 700, 695 (=C-H of mono- and 1,3-disubstituted benzenes).	6.50–7.70 m (24H, CH$_{arom.}$).	231 (4.14) 305 (4.66)	C$_{30}$H$_{24}$N$_2$ (412.53)		87.35 87.05	5.86 5.71	6.79 6.87
1c	3030 (=C-H); 850, 843, 767, 757, 710 (=C-H of mono- and 1,4-disubstituted benzenes).	6.90–7.50 m (24 H, CH$_{arom.}$).	224.4(4.23) 312.5(4.47)	C$_{30}$H$_{24}$N$_2$ (412.53)		87.35 87.05	5.86 5.55	6.79 6.62
1d	3060, 3013 (=C-H); 2970, 2940, 2910 (CH$_3$); 770, 760, 730, 720, 695 (=C-H of 1,2- and 1,3-disubstituted benzenes).	1.85 s (12H, 4CH$_3$); 5.80–6.50 m, 6.80–7.70 m (20H, CH$_{arom.}$).	236 (4.17) 295 (4.61)	C$_{34}$H$_{32}$N$_2$ (468.64)		87.14 86.87	6.88 6.80	5.98 6.11
1e	3025 (=C-H); 2915 (CH$_3$); 765, 708, 693, 688 (=C-H of 1,3-disubstituted benzene).	2.10 s (12H, 4CH$_3$); 6.40–7.50 m (20H, CH$_{arom.}$).	231 (4.20) 305 (4.56)	C$_{34}$H$_{32}$N$_2$ (468.64)		87.14 86.89	6.88 6.81	5.98 5.87
1f	3020 (=C-H); 2915 (CH$_3$); 820, 803, 793, 774, 757, 708, 697, 685 (=C-H of 1,3- and 1,4-disubstituted benzenes).	2.20 s (12H, 4CH$_3$); 6.50–7.20 m (20H, CH$_{arom.}$).	235.0(4.10) 303 (4.64)	C$_{34}$H$_{32}$N$_2$ (468.64)		87.14 86.90	6.88 6.83	5.98 6.09
1g	3000 (=C-H); 2920, 2900 (CH$_3$); 860, 815, 790, 763, 718, 703, 687 (=C-H of 1,3-di- and 1,2,4-trisubstituted benzenes).	1.93 s (12H, 4CH$_3$); 1.97 s (12H, 4CH$_3$); 6.50–7.00 m (16H, CH$_{arom.}$).	233 (4.08) 303 (4.52)	C$_{38}$H$_{40}$N$_2$ (524.75)		86.98 86.68	7.68 7.63	5.34 5.40
1h	3007 (=C-H); 2900 (CH$_3$); 965, 808, 800 (=C-H of 1,4-di- and 1,2,4-trisubstituted benzenes).	1.95 s (3H, CH$_3$); 2.25 s (12H, 4CH$_3$); 6.60–7.20 m (19H, CH$_{arom.}$).	233 (4.10) 303 (4,63)	C$_{35}$H$_{34}$N$_2$ (482.67)		87.10 86.83	7.10 7.04	5.80 5.67
1i	3100 (=C-H); 2950, 2900 (CH$_3$); 870, 860, 810 (=C-H of 1,2,4-trisubstituted benzene).	1.80 s (3H, CH$_3$); 2.03 s (24H, 8CH$_3$); 6.50–7.10 m (15H, CH$_{arom.}$).	233 (4.37) 303 (4.68)	C$_{39}$H$_{42}$N$_2$ (538.77)		86.94 86.68	7.86 7.78	5.20 5.41

For **1d** yield 32,5%, *m.p.*142–143.5 °C (*n*-octane).
For **1e** yield 37,1%, *m.p.* 61–63 °C (*n*-octane).
For **1f** yield 35%, *m.p.* 154.5–156 °C (acetic acid).
For **1g** yield 28%, *m.p.* 129.5–130.5 °C (*n*-octane).
For **1h** yield 45%, *m.p.* 160.5–161.5 °C (*n*-octane).
For **1i** yield 27%, *m.p.* 176.0–177.5 °C (acetic acid).

For the spectral and elemental analyses data of the compounds see Table 2.

Samples Preparation and Electrophotographic Measurements

Two kinds of pigments were used as material for charge generation layers (CGL): bisazopigment – 2,7-bis[3-(2-chlorophenylcarbamoyl)-2-hydroxy-1-naphthylazo]-9-fluorenone was obtained according to the procedure described in [16]; phthalocyanine dye – Y-form oxotitanium phthalocyanine (TiOPc) was synthesized by P. Kadziauskas and coworkers in Vilnius University. Both pigments were dispersed with 30% polyvinylbutyral (PWP-LA, Russia) by sand mill in the proper dissolvers.

CGL were coated on glass substrate with conductive SnO_2 layer by spraying technique. All the substrates for each kind of the pigment were coated by one spraying procedure. This method provided that all the CGL were of the same thickness and possessed equal photogeneration properties. The thickness of the CGL were 0.3 ± 0.015 µm for bisazopigment and 0.8 ± 0.04 µm for TiOPc. The charge transporting layers (CTL) were of 25 ± 1 µm thick and consisted 50% by weigh of investigated compounds **1a**–**i** in a polycarbonate (APEC 9202, Bayer AG) matric. Both components were dissolved in a dichloromethane.The CTL were coated onto CGL by deep coating method and then dried at 80 °C. Such bilayers were charged with negative corone to –1 000 V and exposed to 780 nm (for TiOPc) or 620 nm (for bisazopigment) light. Potential half decay exposure was measured with dynamic electrometer and photosensitivity (S) calculated [20]. The residual potential (U_R), corresponding to exposure equal to 20 half-decay exposures, was also measured.

References

[1] P. Strohriegl, J. V. Gražulevičius in: Handbook of Organic Conductive Molecules and Polymers, H. S. Nalwa (Ed.), John Wiley and Sons, Chichester 1997, Vol. 1, p. 553
[2] K. Nishimura, H. Inada, T. Kobota, Y. Matsui, Y. Shirota, Mol. Cryst. Liq. Cryst. **1992**, *217*, 235
[3] Y. Kanemitsu, Electrophotography **1993**, *32*, 60
[4] H. Kitayama, M. Yokoyama, H. Mikawa, Mol. Cryst. Liq. Cryst. **1981**, *69*, 257
[5] Yoichi To, Yoichi Nishioka (Oki Electric Industry Co., Ltd., Japan) JP01044951, **1989**, Chem. Abstr. **1989**, *111*, 87418z
[6] S. Kutkevicius, A. Stanisauskaite, V. Getautis, A. Railaite, S. Uss, J. Prakt. Chem. **1995**, *337*, 315
[7] W. Ishikawa, H. Inada, H. Nakano, Mol. Cryst. Liq. Cryst. **1992**, *211,* 431
[8] K. Nukada, K. Sata, Y. Akasaki, Electrophotography **1991**, *30*, 16
[9] H. Tanaka, S. Tokito, Y. Taga, A. Okada, Chem. Commun. **1996**, 2175
[10] K. Naito, A. Miura, J. Phys. Chem. **1993**, *97*, 6240
[11] J. Lovie, J. F. Hartwig, A. J. Fry, J. Am. Chem. Soc. **1997**, *119*, 11695
[12] W. Ishikawa, K. Noguchi, Y. Kuwabara, Y. Shirota, Adv. Mater. **1993**, *5*, 559
[13] Y. Zhang, T. Wada, L. Wang, H. Sasabe, Tetrahedron Lett. **1997**, *38*, 1785
[14] H. J. Bolink, C. Arts, V. V. Krasnikov, G. G. Malliaras, G. Hadziioannou, Chem. Mater. **1997**, *9*, 1407
[15] F. Ullmann, Ber. Dtsch. Chem. Ges. **1903**, *36*, 2382
[16] M. Hashimoto, Electrophotography **1986**, *25*, 10
[17] H. O. Wirth, Angew. Makromol. Chem. **1991**, 185/186, 329
[18] C. Haeussermann, Ber. Dtsch. Chem. Ges. **1901**, *34*, 38
[19] C. Haeussermann, E. Bauer, Ber. Dtsch. Chem. Ges. **1899**, *32*, 1912
[20] A. Undzenas, V.Uss, A. Liudkevicius, Lietuvos Fizikos Rinkinys (Vilnius, Lithuanian Physics Journal) **1982**, *22, 94*

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