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Synthesis, Film-Forming Properties, and Thermal and Light Sensitivity of *N,N'*-Bis[4-hydroxy(alkoxy, acyloxy)-3-alkoxyphenylmethylidene]benzene-1,4-diamines

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Abstract—Previously unknown *E,E*-isomeric Schiff bases were synthesized by reaction of *p*-phenylenediamine with 4-hydroxy-3-methoxybenzaldehyde, 3-ethoxy-4-hydroxybenzaldehyde, and their *O*-alkyl and *O*-acyl derivatives in anhydrous methanol. Film-forming properties and thermal and light sensitivity of the products were studied.

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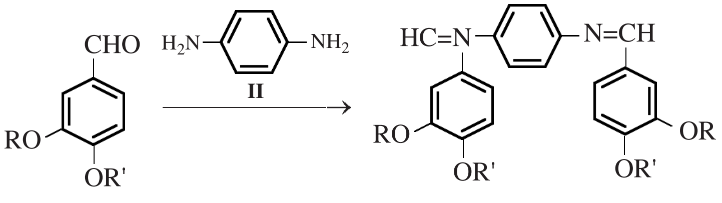
We previously studied film-forming properties and light sensitivity of aromatic Schiff bases which were synthesized from vanillin derivatives and chrysen-2-amine and biphenyl-4-amine [1, 2]. The present communication reports on the synthesis, physical and film-forming properties, and thermal and light sensitivity of new Schiff bases containing two azomethine moieties. These compounds were prepared by condensation of 4-hydroxy-3-methoxybenzaldehyde, 3-ethoxy-4-hydroxybenzaldehyde, and their *O*-alkyl and *O*-acyl derivatives with *p*-phenylenediamine in boiling anhydrous methanol. Previously unknown (*E,E*)-*N,N'*-bis[4-hydroxy(alkoxy, acyloxy)-3-alkoxyphenylmethylidene]benzene-1,4-diamines **IIIa**–**IIIz** and **IVa**–**III**β were isolated in 84–91% yields. The reactions were complete in 0.5 h and required no catalyst, so that labile ester groups in the initial aldehydes remained intact.



I

IIIa–IIIz, IVa–IVβ

III, R = Me, R' = H (**a**), Me (**b**), MeC(O) (**c**), EtC(O) (**d**), PrC(O) (**e**), $Me_2CHC(O)$ (**f**), $Me(CH_2)_6C(O)$ (**g**), $Me(CH_2)_7C(O)$ (**h**), $Me(CH_2)_8C(O)$ (**i**), $Me(CH_2)_{16}C(O)$ (**j**), $H_2C{=}C(Me)C(O)$ (**k**), *cyclo*-$C_6H_{11}C(O)$ (**l**), $C_6H_5CH_2C(O)$ (**m**), $C_6H_5(CH_2)_2 \cdot C(O)$ (**n**), $C_6H_5CH(Me)CH_2C(O)$ (**o**), (*Z*)-$C_6H_5CH{=}C(CN)C(O)$ (**p**), $C_6H_5C(O)$ (**q**), 4-$ClC_6H_4C(O)$ (**r**), 2,4-$Cl_2C_6H_3C(O)$ (**s**), 2,4-$Cl_2C_6H_3OCH_2C(O)$ (**t**), 4-$BrC_6H_4C(O)$ (**u**), 3-$O_2NC_6H_4C(O)$ (**v**), 3,5-$(O_2N)_2C_6H_3C(O)$ (**w**), MeOC(O) (**x**), EtOC(O) (**y**), $MeOC(O)(CH_2)_2C(O)$ (**z**); **IV**, R = Et, R' = H (**a**), Me (**b**), MeC(O) (**c**), EtC(O) (**d**), PrC(O) (**e**), $Me_2CHC(O)$ (**f**), $Me_2CHCH_2C(O)$ (**g**), $Me(CH_2)_4C(O)$ (**h**), $Me(CH_2)_5C(O)$ (**i**), $Me(CH_2)_6C(O)$ (**j**), $Me(CH_2)_7C(O)$ (**k**), $Me(CH_2)_8C(O)$ (**l**), $Me(CH_2)_{11}C(O)$ (**m**), $Me(CH_2)_{16}C(O)$ (**n**), *cyclo*-$C_6H_{11}C(O)$ (**o**), $C_6H_5(CH_2)_2C(O)$ (**p**), $C_6H_5CH(Me)CH_2C(O)$ (**q**), *trans*-$C_6H_5CH{=}CHC(O)$ (**r**), (*Z*)-$C_6H_5CH{=}C(CN)C(O)$ (**s**), 4-$MeC_6H_4C(O)$ (**t**), 2,4-$Cl_2C_6H_3C(O)$ (**u**), 2,4-$Cl_2C_6H_3OCH_2 \cdot C(O)$ (**v**), 3-$O_2NC_6H_4C(O)$ (**w**), 4-$O_2NC_6H_4C(O)$ (**x**), 3,5-$(O_2N)_2C_6H_3C(O)$ (**y**), MeOC(O) (**z**), EtOC(O) (α), $MeOC(O) \cdot (CH_2)_2C(O)$ (β).

Schiff bases **IIIa**–**IIIz** and **IVa**–**IIIβ** are colored (mostly yellow) crystalline substances that are soluble in benzene, chloroform, and acetone and insoluble in methanol, ethanol, and hexane. Compounds **III** and **IV** required no additional purification, for they contained no impurities of initial compounds. Their structure was confirmed by elemental analysis, molecular weight determination by cryoscopy (see table), and IR, UV, and ^{1}H NMR spectroscopy. According to the ^{1}H NMR data, Schiff bases **III** and **IV** were isolated as individual *E,E* isomers [3] with a purity of 97 ± 1%.

The IR spectra of Schiff bases **IIIa**–**IIIz** and **IVa**–**IIIβ** contained absorption bands in the regions 3100–3000 and 870–720 (C–H$_{\text{arom}}$), 2990–2840 (C–H$_{\text{aliph}}$), 1770–1740 (C=O; **IIIc**–**IIIz**, **IVc**–**IVβ**), 1625–1620 (C=N), 1600–1370 (C–C$_{\text{arom}}$), and 1280–1000 cm^{-1} (C–O). The cyano group in molecules **IIIp** and **IVs** gave rise to absorption at 2225–2224 cm^{-1}, and compounds **IIIv**, **IIIw** and **IVv**–**IVy** characteristically showed in the IR spectra absorption bands in the regions 1541–1525 and 1349–1343 cm^{-1} due to stretching vibrations of the nitro groups. The follow-

Yields, melting points, elemental analyses, and molecular weights of Schiff bases **IIIa**–**IIIz** and **IVa**–**IVβ**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			*M*	
			C	H	N		C	H	N	found	calculated
IIIa	89	189–190	70.36	5.48	7.21	$C_{22}H_{20}N_2O_4$	70.20	5.36	7.44	368.7	376.4
IIIb	91	175–176	71.42	6.10	6.82	$C_{24}H_{24}N_2O_4$	71.27	5.98	6.93	397.1	404.5
IIIc	90	206–207	68.03	5.32	5.78	$C_{26}H_{24}N_2O_6$	67.82	5.25	6.08	445.4	460.5
IIId	90	134–135	69.12	5.93	5.50	$C_{28}H_{28}N_2O_6$	68.84	5.78	5.73	460.9	488.5
IIIe	90	133–134	70.01	6.38	5.05	$C_{30}H_{32}N_2O_6$	69.75	6.24	5.42	500.6	516.6
IIIf	91	148–149	70.08	6.32	5.05	$C_{30}H_{32}N_2O_6$	69.75	6.24	5.42	502.2	516.6
IIIg	84	111–112	72.73	7.84	4.12	$C_{38}H_{48}N_2O_6$	72.58	7.69	4.46	617.7	628.8
IIIh	90	97–98	73.29	8.11	3.95	$C_{40}H_{52}N_2O_6$	73.14	7.98	4.26	638.2	656.9
IIIi	91	92–93	73.88	8.32	3.87	$C_{42}H_{56}N_2O_6$	73.65	8.24	4.09	661.9	684.9
IIIj	90	80–81	76.90	9.84	2.83	$C_{58}H_{88}N_2O_6$	76.61	9.75	3.08	880.6	909.3
IIIk	86	174–174	70.57	5.52	5.39	$C_{30}H_{28}N_2O_6$	70.30	5.51	5.47	498.2	512.6
IIIl	89	157–158	72.69	6.86	4.35	$C_{36}H_{40}N_2O_6$	72.46	6.76	4.69	580.8	596.7
IIIm	91	183–184	74.65	5.41	4.30	$C_{38}H_{32}N_2O_6$	74.50	5.26	4.57	587.5	612.7
IIIn	90	158–159	75.16	5.78	4.05	$C_{40}H_{36}N_2O_6$	74.98	5.66	4.37	449.0	460.7
IIIo	90	161–162	75.87	6.21	3.90	$C_{42}H_{40}N_2O_6$	75.43	6.03	4.19	651.7	668.8
IIIp	91	242–243	73.62	4.43	7.87	$C_{42}H_{30}N_4O_6$	73.46	4.40	8.16	658.4	686.7
IIIq	86	229–230	74.17	4.98	4.55	$C_{36}H_{28}N_2O_6$	73.96	4.83	4.79	562.9	584.6
IIIr[a]	90	232–233	66.36	4.19	4.06	$C_{36}H_{26}Cl_2N_2O_6$	66.16	4.01	4.29	634.7	653.5
IIIs[b]	90	215–216	60.04	3.42	3.57	$C_{36}H_{24}Cl_4N_2O_6$	59.85	3.35	3.88	703.6	722.4
IIIt[c]	88	155–156	58.49	3.76	3.23	$C_{38}H_{28}Cl_4N_2O_8$	58.33	3.61	3.58	760.0	782.5
IIIu[d]	91	228–229	58.44	3.64	3.52	$C_{36}H_{26}Br_2N_2O_6$	58.24	3.53	3.77	725.3	742.4
IIIv	90	210–211	64.18	4.02	8.04	$C_{36}H_{26}N_4O_{10}$	64.09	3.88	8.30	655.2	674.6
IIIw	90	267–268	56.73	3.29	10.67	$C_{36}H_{24}N_6O_{14}$	56.55	3.16	10.99	755.8	764.6
IIIx	89	214–215	63.72	5.05	5.36	$C_{26}H_{24}N_2O_8$	63.41	4.91	5.69	481.7	492.5
IIIy	89	174–175	64.80	5.62	5.11	$C_{28}H_{28}N_2O_8$	64.61	5.42	5.38	503.0	520.5
IIIz	90	135–136	63.83	5.45	4.40	$C_{32}H_{32}N_2O_{10}$	63.57	5.33	4.63	584.3	604.6
IVa	88	65–66	71.42	6.09	6.76	$C_{24}H_{24}N_2O_4$	71.27	5.98	6.93	390.2	404.5
IVb	91	182–183	72.41	6.63	6.20	$C_{26}H_{28}N_2O_4$	72.20	6.52	6.48	416.8	432.5
IVc	85	195–196	68.99	5.85	5.57	$C_{28}H_{28}N_2O_6$	68.84	5.78	5.73	467.5	488.5
IVd	90	170–171	69.94	6.24	5.24	$C_{30}H_{32}N_2O_6$	69.75	6.24	5.42	498.4	516.6
IVe	91	152–153	70.75	6.70	4.83	$C_{32}H_{36}N_2O_6$	70.57	6.66	5.14	528.1	544.6
IVf	90	168–169	70.73	6.75	4.87	$C_{32}H_{36}N_2O_6$	70.57	6.66	5.14	530.4	544.6
IVg	89	137–138	71.64	7.21	4.60	$C_{34}H_{40}N_2O_6$	71.31	7.04	4.89	558.6	572.7
IVh	87	132–133	72.00	7.46	4.17	$C_{36}H_{44}N_2O_6$	71.79	7.38	4.66	581.9	600.8
IVi	89	126–127	72.67	7.84	4.16	$C_{38}H_{48}N_2O_6$	72.58	7.69	4.46	610.3	628.8
IVj	90	122–123	73.47	8.13	3.95	$C_{40}H_{52}N_2O_6$	73.14	7.98	4.26	637.0	656.9

Table (Contd.)

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			*M*	
			C	H	N		C	H	N	found	calculated
IVk	90	96–97	73.91	8.29	3.88	$C_{42}H_{56}N_2O_6$	73.65	8.24	4.09	671.7	682.9
IVl	90	85–86	74.36	8.58	3.85	$C_{44}H_{60}N_2O_6$	74.12	8.48	3.93	697.2	713.0
IVm	87	92–93	72.85	8.89	3.06	$C_{50}H_{72}N_2O_6$	72.61	8.77	3.39	804.4	827.1
IVn	90	73–74	77.03	10.02	2.77	$C_{60}H_{92}N_2O_6$	76.88	9.89	2.99	917.5	937.4
IVo	89	176–177	73.24	7.19	4.13	$C_{38}H_{44}N_2O_6$	73.05	7.10	4.48	613.8	624.8
IVp	89	143–144	75.68	6.23	3.96	$C_{42}H_{40}N_2O_6$	75.43	6.03	4.19	645.3	668.8
IVq	90	191–192	75.97	6.51	3.77	$C_{44}H_{44}N_2O_6$	75.84	6.36	4.02	680.2	696.8
IVr	88	193–194	76.14	5.58	3.96	$C_{42}H_{36}N_2O_6$	75.89	5.46	4.21	643.7	664.8
IVs	90	248–249	74.20	4.92	7.57	$C_{44}H_{34}N_4O_6$	73.94	4.79	7.84	694.6	714.8
IVt	89	198–199	75.22	5.81	4.09	$C_{40}H_{36}N_2O_6$	74.98	5.66	4.37	447.0	460.7
IVu[e]	89	210–211	60.97	3.78	3.56	$C_{38}H_{28}Cl_4N_2O_6$	60.82	3.76	3.73	737.1	750.5
IVv[f]	88	176–177	58.56	4.13	3.20	$C_{40}H_{32}Cl_4N_2O_8$	59.28	3.98	3.46	786.3	810.5
IVw	90	240–241	65.20	4.44	7.81	$C_{38}H_{30}N_4O_{10}$	64.95	4.30	7.97	679.4	702.7
IVx	90	265–266	65.15	4.38	7.86	$C_{38}H_{30}N_4O_{10}$	64.95	4.30	7.97	682.5	702.7
IVy	88	303–304	75.86	3.63	10.22	$C_{38}H_{28}N_6O_{14}$	75.58	3.56	10.60	770.5	792.7
IVz	91	202–203	64.69	5.50	5.05	$C_{28}H_{28}N_2O_8$	64.61	5.42	5.38	503.7	520.5
IVα	90	193–194	65.72	5.97	4.88	$C_{30}H_{32}N_2O_8$	65.58	5.88	5.11	527.9	548.6
IVβ	90	148–149	64.76	5.85	4.14	$C_{34}H_{36}N_2O_{10}$	64.55	5.74	4.43	618.8	632.7

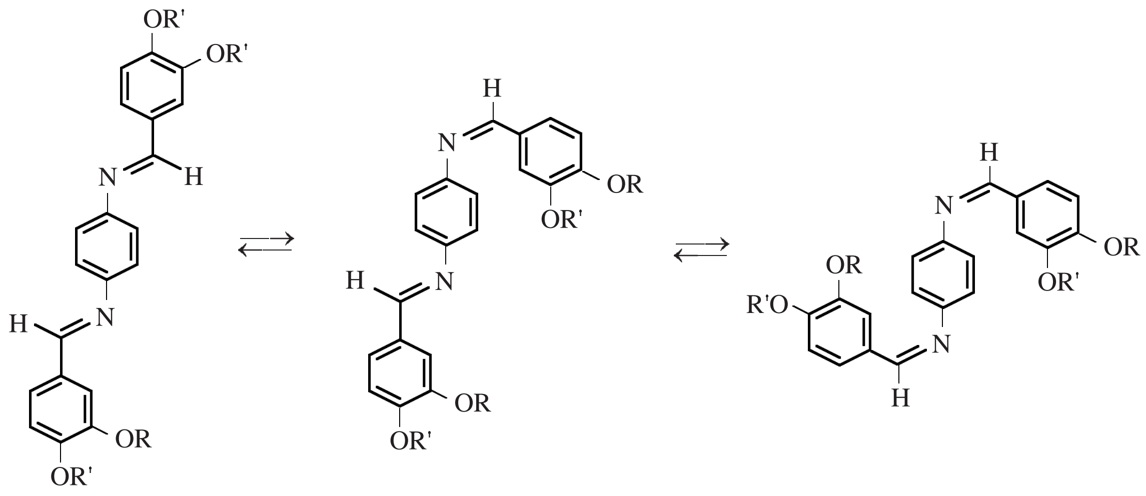
[a] Found Cl, %: 10.60. Calculated Cl, %: 10.85. [b] Found Cl, %: 19.26. Calculated Cl, %: 19.63. [c] Found Cl, %: 17.88. Calculated Cl, %: 18.12. [d] Found Br, %: 21.32. Calculated Br, %: 21.53. [e] Found Cl, %: 18.65. Calculated Cl, %: 18.90. [f] Found Cl, %: 17.18. Calculated Cl, %: 17.50.

ing absorption maxima were observed in the UV spectra of **IIIa**–**IIIz** and **IVa**–**III**β, λ_{max}, nm (log ε): 209 (4.48), 221 (3.38), 273 (4.20), 354 (3.38).

In the ^{1}H NMR spectra of Schiff bases **IIIa**–**IIIz** and **IVb**, protons in the methoxy group resonated as a singlet at δ 3.85–3.92 ppm; ethoxy group in **IVa**–**IV**β gave a triplet at δ 1.35–1.70 ppm (Me) and a quartet at δ 4.00– 4.40 ppm (CH_2). Aromatic proton signals were located in the δ region 7.00–7.80 ppm, and the azomethine HC=N proton resonated as a singlet at δ 8.40–8.50 ppm; the position of the latter signal is typical of *E* isomers of Schiff bases [3].

Some relatively high-melting Schiff bases (mp >100°C, see table) showed thermochromic effect [4] arising from reversible transformation of *E,E* isomer into less thermodynamically stable *Z,Z* isomer prior to melting. This process was accompanied by change of the crystal shape and reduction in the color intensity just before melting. No thermochromic effect was observed for low-melting Schiff bases **IIIh**–**IIIj**, **IVa**, and **IVk**–**IVn**. In order to verify the nature of thermochromic effect observed upon melting, we performed semiempirical MNDO PM3 calculations of heats of formation (ΔH_f) of the *E,E*, *E,Z*, and *Z,Z* isomers of Schiff bases **IIIq** and **IVc** with complete optimization of all bond lengths and bond and dihedral angles using GAMESS program [5]. The following ΔH_f values were obtained (kcal mol^{-1}): *E,E* isomers: –48.8 (**IIIq**), –132.5 (**IVc**); *E,Z* isomers: –46.6 (**IIIq**), –131.7 (**IVc**); *Z,Z* isomers: –46.2 (**IIIq**), –128.4 (**IVc**). Thus, the *E,E* configuration is more stable than *E,Z* (by 0.8–2.2 kcal mol^{-1}) and *Z,Z* (by 2.6–4.1 kcal mol^{-1}). The calculated energy barriers to the transformations of one isomer into another were estimated at 8–12 kcal mol^{-1}. Thus Schiff bases **III** and **IV** attract interest as potential heat-sensitive molecular switches [6].

By thermal vacuum evaporation (TVE) of 0.1-mmol (0.038–0.094-g) samples of powdered Schiff bases **IIIa**–**IIIz** and **IVa**–**III**β we obtained mainly glossy films with a thickness of 0.5–1.6 μm, which had a pale yellow or orange hue and exhibited a good adhesion to various supports (monocrystalline silicon, quartz, pyroceram, polymeric layers, etc.). In most cases, samples evaporated completely or with a small residue (0.1–0.3%). Exceptions were dinitro derivatives **IIIw** and **IVy**; their evaporation was accompanied by decomposition (up to 36%) and formation of a carbon residue. Nevertheless, the IR spectra of the obtained films were similar to those of the corresponding initial



E,E *E,Z* *Z,Z*

samples. The glossiness and transparency of films prepared from all Schiff bases did not changed for a long time (over a month).

The films turned out to be sensitive to UV light in the λ range from 260 to 380 nm. Their exposure to UV light through a photomask gave rise to a latent image, and the subsequent vacuum evaporation at the same temperature as for film deposition resulted in formation of a negative relief pattern. The resolution of films obtained by thermal vacuum evaporation of the examined Schiff base was 1 to 3 μm in optical photolithography.

Using laser ablation lithography (energy exposure up to 150 kJ cm^{-3}), a submicron relief pattern may be generated in TVE films based on the prepared Schiff bases. The films are resistant to atmospheric air and visible light, and they can be used as yellow light filters. They also may be interesting for nanotechnology of organic light-emitting diodes as a buffer layer preventing diffusion of oxygen atoms from transparent anode (ITO film) and reducing the energy barrier to hole injection [12].

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protege-460 spectrometer with Fourier transform. The UV spectra were obtained on a Varian Cary-300 UV-Vis spectrophotometer from 1×10^{-4} M solutions in methanol. The ^{1}H NMR spectra were measured from 5% solutions in $CDCl_3$ on a Tesla BS-587A spectrometer (100 MHz) using tetramethylsilane as internal reference. The elemental compositions were determined with an accuracy of 0.1% on a Vario EL-III Elementar C,H,N,O,S analyzer. Thermal vacuum evaporation was performed using a VUP-4 setup according to the procedure described in [1, 2, 8]; films were deposited from the gas phase onto a silicon support for IR spectroscopy. The deposition process was controlled with the aid of a quartz resonator, and film thickness was measured using an MII-4 Linnick interferometer. The IR spectra of the films deposited onto silicon supports were recorded on a Protege-460 spectrometer.

Initial esters **I** were synthesized according to the procedures described in [9–12]. Benzene-1,4-diamine (**II**) of analytical grade was used (purity 98%, mp 139–140°C).

(*E,E*)-*N,N*'-Bis[4-hydroxy(alkoxy, acyloxy)-3-alkoxyphenylmethylidene]benzene-1,4-diamines IIIa–IIIz and IVa–IIIβ *(general procedure).* A solution of 5 mmol of the corresponding aldehyde **I** and 2.5 mmol of *p*-phenylenediamine (**II**) in 30 ml of anhydrous methanol was heated for 0.5 h under reflux. The hot solution was filtered through a folded filter paper, the filtrate was cooled and left to stand for 10–15 h at 5°C, and the precipitate was filtered off through a glass filter, washed with a small amount of methanol, and dried in air.

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