PREPARATION AND PROPERTIES OF ISOMERIC *N*-(4-SUBSTITUTED BENZYLIDENE)-4-ETHYNYLANILINES AND 4-SUBSTITUTED *N*-(4-ETHYNYLBENZYLIDENE)ANILINES

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4-Substituted *N*-(4-ethynylbenzylidene)anilines (4-HC≡C–C_6H_4–CH=N–C_6H_4–4-R; R = Me, *t*-Bu, OMe, F, Cl, Br, I, CF_3 and NO_2) have been prepared by condensation of 4-ethynylbenzaldehyde with appropriate anilines under mild conditions in good yields. The products obtained were fully characterized by GC-MS, IR, NMR and UV-VIS spectroscopies and their properties were compared with a series of 4-ethynyl-*N*-(4-substituted benzylidene)anilines (4-HC≡C–C_6H_4–N=CH–C_6H_4–4-R; R = H, Me, *t*-Bu, F, Br, NO_2, CN, NMe_2). The influence of substituent R on spectroscopic characteristics is discussed.

Key words: Alkynes; Schiff bases; Imines; Ethynylated benzylideneanilines; Polyacetylenes; Polymerization; Mass spectrometry; NMR spectroscopy; Electronic spectroscopy.

Although benzylideneanilines with a variety of substituents in both benzene rings have been known and intensively studied for a long time, ethynylated benzylideneanilines were virtually unknown until recently. An increasing interest in new materials for electronics and optics based on organic molecules with long high-conjugated hydrocarbon chains awoke an interest in the synthesis of starting compounds for their preparation. Among other things, acetylene-terminated aromatic Schiff bases have also aroused attention. Diethynylated Schiff bases prepared by condensation of phthalaldehydes with ethynylaniline were polymerized by an oxidative coupling of the acetylenic groups to yield linear polymers which contain alternating aromatic Schiff base and diacetylene repeat units[1]. From difunctional phenylethynyl-terminated Schiff bases synthesized by condensation of phenylethynylbenzaldehyde with diaminobenzene, new electrically conducting polymers were prepared by heat treatment[2]. A series of mostly new 4-ethynyl-*N*-benzylideneanilines (4-HC≡C–C_6H_4–N=CH–C_6H_4–4-R; R = H, *t*-Bu, F, Br, NO_2, CN, NMe_2) have been prepared and polymerized[3]. Using Rh-based polymerization catalysts, new polyacetylenes with a conjugated polyene main chain and *N*-benzylideneaniline pendant groups were obtained. Ethynylated Schiff bases with strong dipole moments may also find application in preparation of low-molecular weight compounds for non-linear optics. For example, Whittall and coworkers prepared 4-HC≡C–C_6H_4–N=CH–C_6H_4–4-NO_2 and coupled it with cyclopentadienyl ruthenium complex in order to obtain a new complex with enhanced quadratic hyperpolarizability[4].

Whittall and coworkers prepared 4-HC≡C–C_6H_4–N=CH–C_6H_4–4-NO_2 by refluxing 4-ethynylaniline with 4-nitrobenzaldehyde in ethanol. They also claimed[4] that attempts to isolate “inverse” compound 4-HC≡C–C_6H_4–CH=N–C_6H_4–4-NO_2 were unsuccessful due to its rapid hydrolysis. In the previous paper[3] we showed that 4-ethynyl-*N*-(4-substituted benzylidene)anilines (4-HC≡C–C_6H_4–N=CH–C_6H_4–4-R; R= *t*-Bu, F, Br, NO_2, CN, NMe_2) can be easily prepared without heating just by mixing of 4-ethynylaniline with equimolar amount of an appropriate aldehyde in methanol at room temperature. This contribution reports on the preparation of *N*-(4-ethynylbenzylidene)anilines (4-HC≡C–C_6H_4–CH=N–C_6H_4–4-R; labelled as **2** series) and discusses their spectroscopic characteristics in comparison with “inverse” 4-ethynyl-*N*-benzylideneanilines (4-HC≡C–C_6H_4–N=CH–C_6H_4–4-R; labelled as **1** series).

EXPERIMENTAL

Chemicals

4-Methyl-, 4-*tert*-butyl-, 4-methoxy-, 4-fluoro-, 4-chloro-, 4-bromo-, 4-iodo-, 4-nitro- and 4-(trifluoromethyl)aniline as well as 4-methylbenzaldehyde were purchased from Aldrich and were used without any purification. 4-Ethynylaniline and 4-ethynylbenzaldehyde were prepared according to literature[5] by reaction of (trimethylsilyl)acetylene with iodoaniline and bromobenzaldehyde, respectively. The final products were purified by sublimation *in vacuo*. Methanol (p.a., Lachema, Czech Republic) was used as obtained. Tetrahydrofuran (THF) (Riedel deHaen, 99.5%+) was distilled from CaH_2 and CuCl.

Preparation of Ethynylated Schiff Bases – General Procedure

Starting aldehyde (1 mmol) was mixed with starting amine (1 mmol) in methanol (2–4 ml; the amount just necessary to dissolve both components). After some time (5–20 min), the first crystals of the product appeared. After 3 h, a yellow, microcrystalline precipitate was separated, washed with a small amount of methanol and dried to the constant weight (at ambient temperature). From mother liquor, second crop was obtained by distilling off the solvent and recrystallization of the product from methanol. In the case of Schiff bases with F and CF_3 substituents which crystallized with difficulty from the reaction mixture, solvent was simply evaporated after 2 h of the reaction and a slightly yellow product was dried *in vacuo* to the constant weight (ambient temperature). The purity of the products was 97–99% (GC-MS).

4-Ethynyl-N-(4-methylbenzylidene)aniline (**1a**). Yield 58%, m.p. 94–97 °C. MS, *m/z* (%): 219 ($M^{+\bullet}$, 100), 218 ($(M - H)^+$, 90), 203 (5), 128 (8), 102 (10), 101 (41), 91 (19), 75 (20). UV-VIS (THF), λ_{max}, nm: 277 (ε = 22 000), 328 (ε = 16 000). IR (KBr), ν_{max}, cm^{-1}: 3 266 (s, ν(≡C–H)), 2 100 (w, ν(C≡C)), 1 626 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 2.42 s, 3 H (CH_3); 3.09 s, 1 H (H1); 7.14 d, *J* = 8.4, 2 H (H5); 7.28 d, *J* = 8.6, 2 H + 7.79 d, *J* = 8.6, 2 H (H10, H11); 7.41 d, *J* = 8.4, 2 H (H4); 8.39 s, 1 H (H8). ^{13}C NMR ($CDCl_3$): 21.63 (CH_3), 77.22 (C1), 83.61 (C2), 119.26 (C3), 120.92 (C5), 128.92 + 129.54 (C10 + C11), 133.06 (C4), 133.40 (C9), 142.22 (C12), 152.53 (C6), 160.81 (C8). For $C_{16}H_{13}N$ (219.3) calculated: 87.64% C, 5.99% H, 6.39% N; found: 87.37% C, 6.36% H, 6.21% N.

N-(4-Ethynylbenzylidene)-4-methylaniline (**2a**). Yield 63%, m.p. 94–96 °C. MS, *m/z* (%): 219 ($M^{+\bullet}$, 100), 218 ($(M - H)^+$, 70), 204 ($(M - CH_3)^+$, 5), 203 (5), 118 (8), 102 (6), 101 (2), 91 (20), 75 (2). UV-VIS (THF), λ_{max}, nm: 286 (ε = 21 000), 328 (ε = 13 000). IR (KBr), ν_{max}, cm^{-1}: 3 245 (s, ν(≡C–H)), 2 100 (w, ν(C≡C)), 1 623 (s, ν(N=C)).^{1}H NMR ($CDCl_3$): 2.37 s, 3 H (CH_3); 3.21 s, 1 H (H1); 7.15 + 7.20 m, *J* = 8.1, 4 H (H10, H11); 7.58 d, *J* = 8.4, 2 H (H4); 7.85 d, *J* = 8.4, 2 H (H5); 8.45 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 20.99 (CH_3), 79.28 (C1), 83.30 (C2), 120.84 (C10), 124.75 (C3), 128.49 (C5), 129.80 (C11), 132.46 (C4), 136.19 + 136.53 (C6 + C12), 149.09 (C9), 158.34 (C7). For $C_{16}H_{13}N$ (219.3) calculated: 87.64% C, 5.99% H, 6.39% N; found: 87.34% C, 6.27% H, 6.33% N.

N-(4-Ethynylbenzylidene)-4-tert-butylaniline (**2b).** Yield 62%, m.p. 107–108 °C. MS, *m/z* (%): 261 ($M^{+\bullet}$, 26), 246 ($(M - CH_3\ )^+$, 72), 218 (8) , 204 ($(M - C_4H_9)^+$, 6), 128 (7), 127 (8), 109 (33), 102 (30), 101 (36), 77 (100). UV-VIS (THF), λ_{max}, nm: 287 (ε = 22 000), 330 (ε = 14 000). IR (KBr), ν_{max}, cm^{-1}: 3 290 (s, ν(≡C–H)), 2 100 (w, ν(C≡C)), 1 617 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 1.34 s, 9 H (*t*-Bu); 3.21 s, 1 H (H1); 7.18 d, *J* = 8.4, 2 H (H10); 7.42 d, *J* = 8.4, 2 H (H11); 7.58 d, *J* = 8.3, 2 H (H4); 7.86 d, *J* = 8.3, 2 H (H5), 8.46 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 31.41 (Me in *t*-Bu), 34.52 (quaternary C in *t*-Bu), 79.25 (C1), 83.33 (C2), 120.56 (C10), 124.74 (C3), 126.05 (C11), 128.49 (C5), 132.44 (C4), 136.59 (C6), 149.01 + 149.46 (C9 + C12), 158.41 (C7). For $C_{19}H_{19}N$ (261.4) calculated: 87.31% C, 7.33% H, 5.36% N; found: 87.02% C, 7.33% H, 5.36% N.

N-(4-Ethynylbenzylidene)-4-fluoroaniline (**2c**). Yield 65%, m.p. 86–88 °C. MS, *m/z* (%): 223 ($M^{+\bullet}$, 100), 222 ($(M - H)^+$, 98), 194 (2), 128 (2), 122 (14), 102 (13), 101 (17), 95 (45), 75 (25). UV-VIS (THF), λ_{max}, nm: 286 (ε = 19 000), 324 (ε = 12 000). IR (KBr), ν_{max}, cm^{-1}: 3 294 (s, ν(≡C–H)), 2 100 (w, ν(C≡C)), 1 624 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 3.22 s, 1 H (H1); 7.09 m, *J* = 8.7, *J*(H,F) = 8.7, 2 H (H11); 7.21 m, *J* = 8.7, *J*(H,F) = 5.1, 2 H (H10); 7.59 d, *J* = 8.3, 2 H (H4), 7.85 d, *J* = 8.3, 2 H (H5); 8.43 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 79.45 (C1); 83.22 (C2); 115.92, *J*(C,F) = 22.5 (C11); 122.35, *J*(C,F) =8.3 (C10); 125.06 (C3); 128.55 (C5); 132.51 (C4); 136.26 (C6); 147.71, *J*(C,F) = 2.9 (C9); 158.87, *J*(C,F) = 1.4 (C7); 161.44, *J*(C,F) = 245.4 (C12). HR MS, for $C_{15}H_{10}FN$ ($M^{+\bullet}$) calculated: 223.0797, found: 223.0800.

N-(4-Ethynylbenzylidene)-4-bromoaniline (**2d**). Yield 71%, m.p. 124–125 °C. MS, *m/z* (%): 283 ($M^{+\bullet}$, 100), 282 ($(M - H)^+$, 74), 182 (6), 155 (28), 102 (49), 101 (23), 75 (40). UV-VIS (THF), λ_{max}, nm: 288 (ε = 25 000), 329 (ε = 16 000). IR (KBr), ν_{max}, cm^{-1}: 3 255 (s, ν(≡C–H)), 1 615 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 3.23 s, 1 H (H1); 7.09 d, *J* = 8.7, 2 H + 7.51d, *J* = 8.7, 2 H (H10 +

H11); 7.59 d, *J* = 8.4, 2 H (H4); 7.85 d, *J* = 8.4, 2 H (H5); 8.41 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 79.62 (C1), 83.14 (C2), 119.64 (C12), 122.57 (C10), 125.22 (C3), 128.65 (C5), 132.23 + 132.51 (C4 + C11), 136.03 (C6), 150.61 (C9), 159.55 (C7). For $C_{15}H_{10}BrN$ (284.2) calculated: 63.40% C, 3.55% H, 28.20% Br, 4.93% N; found: 63.02% C, 4.01% H, 28.42% Br, 4.73% N.

N-(4-Ethynylbenzylidene)-4-nitroaniline (**2e**). Yield 41%, m.p. 203–205 °C. MS, *m/z* (%): 250 ($M^{+\bullet}$, 100), 249 ($(M - H)^+$, 48), 220 ($(M - NO)^+$, 16), 203 (16), 191 (5), 176 (13), 102 (10), 101 (6), 76 (26). UV-VIS (THF), λ_{max}, nm: 311, 334 (ε = 12 000). IR (KBr), ν_{max}, cm^{-1}: 3 233 (s, ν(≡C–H)), 2 095 (w, ν(C≡C)), 1 613 (s, ν(N=C)).^{1}H NMR ($CDCl_3$): 3.27 s, 1 H (H1); 7.26 d, *J* = 8.8, 2 H + 8.28 d, *J* = 8.8, 2 H (H10 + H11); 7.62 d, *J* = 8.2, 2 H (H4); 7.89 d, *J* = 8.2, 2 H (H5); 8.42 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 80.15 (C1), 82.95 (C2), 121.24 (C10), 125.06 (C11), 126.09 (C3), 129.05 (C5), 132.63 (C4), 135.39 (C6), 145.63 (C12), 157.50 (C9), 161.59 (C7). For $C_{15}H_{10}N_2O_2$ (250.3) calculated: 71.98% C, 4,03% H, 11.19% N; found: 71.07% C, 4.51% H, 11.19% N.

N-(4-Ethynylbenzylidene)-4-methoxyaniline (**2f**). Yield 65%, m.p. 146–149 °C. MS, *m/z* (%): 235 ($M^{+\bullet}$, 100), 234 ($(M - H)^+$, 12), 220 ($(M - CH_3)^+$, 80), 191 (15), 165 (8), 139 (5), 102 (1), 101 (2). UV-VIS (THF), λ_{max}, nm: 286 (ε = 18 000), 350 (ε = 15 000). IR (KBr), ν_{max}, cm^{-1}: 3 245 (s, ν(≡C–H)), 2 100 (w, ν(C≡C)), 1 620 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 3.21 s, 1 H (H1); 3.83 s, 3 H (CH_3); 6.93 d, *J* = 9.0, 2 H (H11); 7.25 d, *J* = 9.0, 2 H (H10); 7.57 d, *J* = 8.3, 2 H (H4); 7.85 d, *J* = 8.3, 2 H (H5); 8.47 s, 1 H (H7).^{13}C NMR ($CDCl_3$): 55.46 (CH_3), 79.20 (C1), 83.33 (C2), 114.39 (C11), 122.26 (C10), 124.51 (C3), 128.33 (C5), 132.43 (C4), 136.63 (C6), 144.47 (C9), 157.00 (C7), 158.52 (C12). For $C_{16}H_{13}NO$ (235.3) calculated: 81.67% C, 5.58% H, 5.95% N; found: 81.73% C, 6.26% H, 5.96% N.

N-(4-Ethynylbenzylidene)-4-chloroaniline (**2g**). Yield 69%, m.p. 106–108 °C. MS, *m/z* (%): 239 ($M^{+\bullet}$, 100), 238 ($(M - H)^+$, 86), 138 (10), 111 (40), 102 (18), 101 (14), 75 (36). UV-VIS (THF), λ_{max}, nm: 286 (ε = 27 000), 330 (ε = 17 000). IR (KBr), ν_{max}, cm^{-1}: 3 255 (s, ν(≡C–H)), 1 616 (s, ν(N=C)).^{1}H NMR ($CDCl_3$): 3.22 s, 1 H (H1); 7.15 d, *J* = 8.8, 2 H + 7.36 d, *J* = 8.8, 2 H (H10 + H11); 7.58 d, *J* = 8.3, 2 H (H4); 7.85 d, *J* = 8.3, 2 H (H5); 8.41 s, 1 H (H7).^{13}C NMR ($CDCl_3$): 79.58 (C1), 83.16 (C2), 122.19 (C10), 125.20 (C3), 128.64 + 129.27 (C5 + C11), 132.50 (C4), 136.07 (C6), 150.12 (C9), 159.48 (C7). For $C_{15}H_{10}ClN$ (239.7) calculated: 75.16% C, 4.21% H, 14.79% Cl, 5.84% N; found: 75.02% C, 4.61% H, 14.61% Cl, 5.79% N.

N-(4-Ethynylbenzylidene)-4-iodoaniline (**2h**). Yield 71%, m.p. 159–161 °C. MS, *m/z* (%): 331 ($M^{+\bullet}$, 100), 330 ($(M - H)^+$, 57), 230 (4), 203 (19), 102 (14), 101 (3), 76 (26). UV-VIS (THF), λ_{max}, nm: 288 (ε = 32 000), 333 (ε = 21 000). IR (KBr), ν_{max}, cm^{-1}: 3 250 (s, ν(≡C–H)), 1 615 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 3.23 s, 1 H (H1); 6.96 d, *J* = 8.7, 2 H + 7.70 d, *J* = 8.7, 2 H (H10 + H11); 7.58 d, *J* = 8.3, 2 H (H4); 7.85 d, *J* = 8.3, 2 H (H5); 8.40 s, 1 H (H7). ^{13}C NMR ($CDCl_3$): 79.63 (C1), 83.16 (C2), 90.67 (C12), 122.93 (C10), 125.26 (C3), 128.68 (C5), 132.52 (C4), 136.05 (C6), 138.23 (C11), 151.33 (C9), 159.60 (C7). For $C_{15}H_{10}IN$ (331.2) calculated: 54.40% C, 3.04% H, 4.23% N; found: 54.06% C, 3.37% H, 4.15% N.

N-(4-Ethynylbenzylidene)-4-trifluoromethylaniline (**2i**). Yield 79%, m.p. 96–99 °C. MS, *m/z* (%): 273 ($M^{+\bullet}$, 100), 272 ($(M - H)^+$, 96), 254 ($(M - F)^+$, 5), 204 ($(M - CF_3)^+$, 3), 172 (8), 145 (48), 102 (16), 101 (12), 75 (14). UV-VIS (THF), λ_{max}, nm: 288 (ε = 23 000), 324 shoulder. IR (KBr), ν_{max}, cm^{-1}: 3 300 (s, ν(≡C–H)), 1 630 (s, ν(N=C)). ^{1}H NMR ($CDCl_3$): 3.24 s, 1 H (H1); 7.25 d, *J* = 8.2, 2 H (H10); 7.60 d, *J* = 8.4, 2 H (H4); 7.65 d, *J* = 8.2, 2 H (H11); 7.87 d, *J* = 8.4, 2 H (H5); 8.41 s, 1 H (C7). ^{13}C NMR ($CDCl_3$): 79.81 (C1); 83.07 (C2); 120.95 (C10); 124.23, *J*(C,F) = 272.0 (CF3); 125.60 (C3); 126.35, *J*(C,F) =3.5 (C11); 127.96, *J*(C,F) = 32.3 (C12);

128.28 (C5); 132.56 (C4); 135.78 (C6); 154.83 (C9); 160.84 (C7). HR MS, for $C_{16}H_{10}F_3N$ ($M^{+\bullet}$) calculated: 273.0762, found: 273.0764.

Preparation and characterization of *N*-(4-*tert*-butylbenzylidene)-4-ethynylaniline (**1b**), *N*-(4-fluorobenzylidene)-4-ethynylaniline (**1c**), *N*-(4-bromobenzylidene)-4-ethynylaniline (**1d**), *N*-(4-nitrobenzylidene)-4-ethynylaniline (**1e**), *N*-(4-dimethylaminobenzylidene)-4-ethynylaniline (**1f**), *N*-(4-cyanobenzylidene)-4-ethynylaniline (**1g**) and *N*-(benzylidene)-4-ethynylaniline (**1h**) are described elsewhere[3]. Yields (%): 64 (**1b**), 86 (**1c**), 68 (**1d**), 68 (**1e**), 42 (**1f**), 87 (**1g**), 80 (**1h**).

Techniques

GC-MS analyses were performed using (i) a Hewlett–Packard gas chromatograph 5890 II with a mass spectrometric detector 5971A equipped with a high-resolution capillary column DB-5 (30 m) and (ii) a Varian 3400 gas chromatograph with an SPB-5 capillary column (30 m) interfaced to Finigan MSAT INCOS 50 mass spectrometer. HR MS analysis was made using MS VG 7070E (double focusing, 6 kV, peak match method, perfluorohydrocarbons as internal standard, resolution 10 000). IR spectra were recorded on a Specord 75 IR spectrometer in KBr pellets (only characteristic bands are given). UV-VIS spectra were recorded on a Hewlett–Packard HP89500 spectrometer in THF.

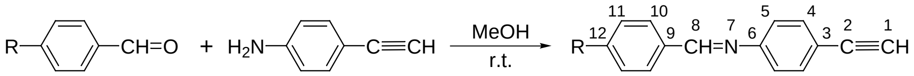
^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Varian Unity-200 NMR spectrometer. Hexamethyldisilane was added as an internal reference for ^1H spectra (δ 0.04), ^{13}C NMR spectra were referenced to the central line of the solvent triplet (δ 76.99). Fluorinated compounds **2c** and **2i** were measured on Varian Unity-500 spectrometer to differenciate between carbon chemical shifts and carbon–fluorine spin-spin couplings. ^{13}C DEPT-editing for multiplicity selected subspectra and chemical shifts calculation assuming additivity of contributions by particular substituents were applied to ^{13}C spectra interpretation. Chemical shifts of benzylidene ring of *N*-(4-ethynylbenzylidene)anilines were calculated by adding of ethynyl-induced contributions of chemical shifts in phenylacetylene to chemical shifts of corresponding *N*-benzylideneanilines[6]. Low sensitivity of chemical shifts of the benzylidene ring on the substituents of the adjacent aniline ring facilitated the assignments. Finally, the assignment was proved for **2i** by a ^{13}C-$\{^1H\}$ selective decoupling of -CH=N- and HC≡C- proton combined with ^{13}C monoresonance experiment. The assignment was done under assumption that $^4J(C4,HC\equiv) > {}^5J(C5,HC\equiv)$ and $^3J(C5,HC{=}N) > {}^4J(C4,HC{=}N)$. In fact, it was found $^5J(C5,HC\equiv) \approx {}^4J(C4,HC{=}N) \approx 0$. ^{13}C chemical shifts of aniline ring of **2a**, **2c**, **2e**–**2g** were found to be the same as in the case of non-ethynylated compounds[6]. For **2b**, **2d**, **2h** and **2i**, the shifts calculated by adding of substituent-induced contributions of corresponding monosubstituted benzenes[7] to the chemical shifts of C_6H_5–CH=N–C_6H_5 were in a good agreement with the data observed, except for C12 carbon of **2i**, where the J(C,F) spin-spin couplings were used for the assignment. For interpretation of aromatic parts of ^1H NMR spectra, a homonuclear selective decoupling was used. Chemical shifts of H4 and H5 obtained by HETCOR for **2b**, **2f** and **2i** were used for the assignment of benzylidene protons of the remaining compounds. Only for **2a** and **2c**, simulation of ^1H NMR spectra was necessary to get exact values of chemical shifts and spin-spin coupling constants. Values of homonuclear proton spin-spin coupling constants of remaining compounds were extracted directly from the ^1H NMR spectra.

The laser kinetic spectrometer (Applied Photophysics) and the details of procedures for measuring the emission and time-resolved absorption spectra have been described elsewhere[8,9]. Transient species were generated by a Lambda Physik LPX 205 XeCl laser (excitation wavelength 308 nm, pulse length 20 ns, energy 10–20 mJ/pulse). A 250-W xenon lamp (Optical Radiation Corporation, U.S.A.) was used as a source of light for absorption spectroscopy.

Elemental analysis was made by Laboratory of Organic Elemental Analysis of the Prague Institute of Chemical Technology.

RESULTS AND DISCUSSION

Ethynylated benzylideneanilines have been prepared (i) by condensation of 4-ethynylaniline with 4-substituted benzaldehydes (Scheme 1, series **1**) and (ii) by condensation of 4-ethynylbenzaldehyde with 4-substituted anilines (Scheme 2, series **2**).

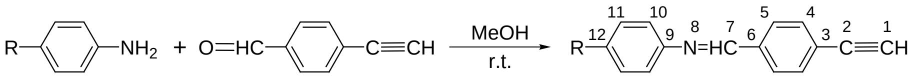


1

1	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R	CH_3	*t*-Bu	F	Br	NO_2	CN	$N(CH_3)_2$

SCHEME 1

Condensation proceeded in methanol at laboratory temperature. In most cases, the products precipitated directly from the reaction mixture. The pure products consisted of yellow or orange microcrystalline solids, stable in air and soluble in benzene, chloroform and THF (dried by conventional methods).



2

2	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
R	CH_3	*t*-Bu	F	Br	NO_2	OCH_3	Cl	I	CF_3

SCHEME 2

Intensive molecular peaks are characteristic of mass spectra of ethynylated benzylideneanilines of both series. Except for **2b**, molecular peak is the most intensive peak in the spectrum. Mass spectral fragmentation of benzylideneaniline was studied by Srzic *et al.*[10]. Under electron impact, molecular ions undergo the following fragmentation processes: (a) loss of hydrogen, (b) cleavage of the bonds adjacent to the C=N group, (c) cleavage of C=N group, (d) skeletal rearrangement with a subsequent loss of

$H^\bullet$, HCN and $H^\bullet$ and leading to the biphenylene cation. It can be seen from mass spectra that ethynylated benzylideneanilines generally obey the fragmentation scheme by Srzic *et al.*: (i) $[M - H]^+$ ions have been observed in all spectra except for **2b**, (ii) peaks 101 and 102 corresponding to the fragment ions $[HC{\equiv}C{-}C_6H_4]^+$ and $[HC{\equiv}C{-}C_6H_5]^+$ are also of high abundance (in particular peak 101 in series **1**) in addition to the low peak of 128 (visible only in several spectra) corresponding to the $[HC{\equiv}C{-}C_6H_4NCH]^+$ and $[HC{\equiv}C{-}C_6H_4CNH]^+$, (iii) fragment ions $[C_6H_5R]^+$ can be easily followed in spectra of methyl and halogen derivatives **1a**, **2a**, **2c**, **2d**, **2g**, **2h**, **2i**, (iv) the $[M - H - HNC - H]^+$ ions have been detected in spectra of fluoro derivatives **1c** and **2c**. On the other hand, the cleavage of C=N bond was not evidenced in our spectra.

In IR spectra, a strong ν(≡C–H) vibration band between 3 230 and 3 300 cm^{-1} and strong ν(C=N) vibration band in the region from 1 615 to 1 630 cm^{-1} are characteristic of ethynylated benzylideneanilines. The ν(C≡C) vibration band appears at about 2 100 cm^{-1}; it is very weak and in some cases it lies below the detection limit.

NMR spectra of benzylideneanilines have been intensively studied by several groups[6,11–13]. These studies helped to prove that benzylidenanilines generally adopt a non-planar structure with the twist angle (dihedral angle between the aniline ring and the plane of azomethine fragment) depending on electronic and steric properties of substituents[12,13]. NMR observations also indicate that the conjugation between benzylidene and aniline rings occurs at considerable extent even in their non-planar conformation[11]. The correlations between electron-withdrawing and electron-releasing abilities of substituents in both benzylidene and aniline rings and chemical shifts of azomethine carbons were also established[11]. NMR spectra of ethynylated benzylideneanilines show that the influence of ethynyl group on distant atoms in the molecule is rather low and the measured data do not much differ from the data given in the literature for similar benzylideneanilines lacking the ethynyl function. The influence of ethynyl substituent on azomethine carbon can be seen from Table I, where the azomethine carbon chemical shifts of some ethynylated compounds are compared with literature data[11] for corresponding non-ethynylated compounds $C_6H_5{-}N{=}CH{-}C_6H_4{-}R$ (series **I**) and $C_6H_5{-}CH{=}N{-}C_6H_4{-}R$ (series **II**). Slight systematic shifts to the higher δ as a result of introduction of ethynyl group in the 4-position of aniline ring and to the lower δ caused by similar ethynylation of the benzylidene ring can be observed. Therefore, the effect of ethynyl group on the CH=N bond polarization is inverse in **1** and **2** series.

As the reactivity of the ethynyl group is essential for applications of ethynylated benzylideneanilines as special monomers, the following discussion of NMR spectra is focused on chemical shifts in this group. The effect of R substituent on chemical shift δ of the ethynyl proton is shown in Fig. 1. For evaluation of electronic properties of substituents, Hammett parameter σ taken from literature[14] has been used. Almost linear increase in δ with increasing σ is clearly seen for both **1** and **2** compounds. The shifts for the **2** series are about 0.1 ppm higher in comparison with the **1** series, indi-

TABLE I
^{13}C NMR chemical shifts of azomethine carbon (in ppm) for ethynylated benzylideneanilines of the **1** and **2** series (δ_1, δ_2) and for corresponding non-ethynylated compounds of the **I** and **II** series (δ_I, δ_{II})

R	δ_1	δ_I	δ_2	δ_{II}
NMe_2	160.64	160.12	–	–
MeO	–	–	157.00	158.36
H	160.87	160.31	–	–
Me	160.81	160.15	158.34	159.45
NO_2	157.91	157.25	161.59	162.59

Data for non-ethynylated compounds are taken from ref.[11], data for **1** compounds from ref.[3]

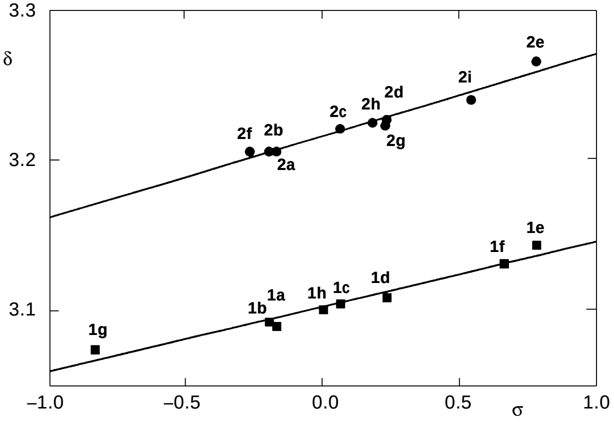


FIG. 1
The dependence of chemical shift of acetylenic proton (δ) on Hammett constant σ for R substituent in **1** (■) and in **2** (●)

cating a generally higher acidity of the ethynyl group in the **2** series. The dependences of ^{13}C NMR chemical shifts of C1 and C2 carbons on σ for both series of compounds are given in Fig. 2. All dependences here can be described as nearly linear: for terminal carbon, δ increases with increasing σ, for internal carbon, a slight decrease in δ with increasing σ can be observed. For terminal carbons, δ values of the **2** compounds are about 2 ppm higher than those of the **1** compounds, for internal carbons, the differences between δ values of the corresponding **1** and **2** compounds are nearly negligible. This indicates that (i) the electrophilicity of C1 carbon is higher in compounds **2** than in compounds **1** (probably the incorporation of the nitrogen electron lone pair into the ethynylphenyl conjugation system decreases the electrophilicity of the terminal carbon of **1** compounds), (ii) the polarity of the C≡C bond in compounds **1** is higher in comparison with that of the C≡C bond in compounds **2** (as it can be seen from the differences between chemical shifts of C1 and C2 carbons) and (iii) the electrophilicity of the C1 carbon as well as the C≡CH bond polarity in both series of compounds may be easily tuned by introduction of a proper electron releasing/withdrawing substituent to the 4-position of the neighbouring ring (probably due to a considerable degree of conjugation between aniline and benzylidene part of molecule).

In the UV-VIS region, benzylideneanilines are known to exhibit two intensive absorption bands: (i) the E_2 band, which is characteristic of the $C_6H_5CH{=}N$ fragment and is interpreted as a transition to a charge transfer

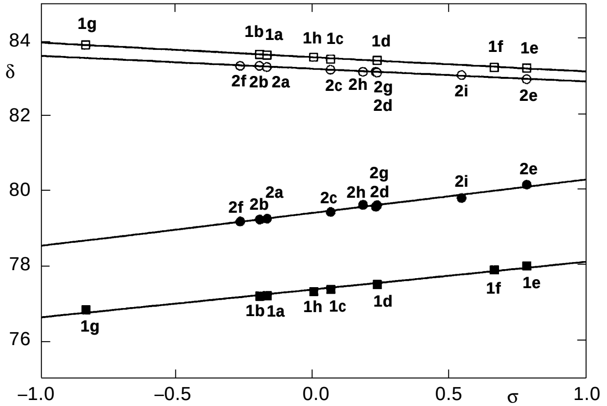


FIG. 2

The dependence of chemical shifts of acetylenic carbons (δ) on Hammett constant σ for R substituent in **1** (■ terminal carbon, ❐ internal carbon) and in **2** (● terminal carbon, ❍ internal carbon) state in which the benzylidene ring is an electron donor and the azomethine group an electron acceptor and (ii) the K band with a maximum usually at a longer wavelength, which is assigned to the π→π* transition extending over the whole molecule[15,16]. The positions and intensities of these bands vary with substituents and also reflect the conformation of the molecule (twist angle)[17]. We have found that UV-VIS absorption spectra of ethynylated benzylideneanilines display the same band pattern. Spectra of **1a**, **1c**, **2a** and **2c** are given in Fig. 3 as typical examples. In the series **1**, the E_2 band has a maximum between 268 and 280 nm. In the series **2**, this maximum appears at higher wavelengths, between 286 and 311 nm. No relation between the E_2 band maximum and the electronegativity of R substituent was found. In both series, the K band appears in the same region between 324 and 354 nm. Only for the **1** series, a slight shift of this maximum with increasing substituent electronegativity can be seen (324 (*t*-Bu), 324 (H), 330 (Br), 340 (CN), 354 (NO_2)).

Fluorescence spectra (in THF) of **1e**–**1g** and compounds of the series **2** have weak maxima at about 400 nm (see Fig. 4, curve *1* for **2c**, as an example). In contrast, fluorescence spectra of **1a**–**1d** exhibit bands at about 500 nm (see Fig. 4, curve *2* for **1c**); the positions of these bands are not affected by substituents R (Scheme 1) and the band intensity decreases in the following order: **1c** (R = F) >> **1d** (Br) > **1b** (*t*-Bu) >> **1a** (Me). A similar Stokes shift to the green region was found earlier for benzylidenaniline substituted with the $N(CH_3)_2$ and NO_2 groups[18]. For **1c**, **1d** and **1b**, formation

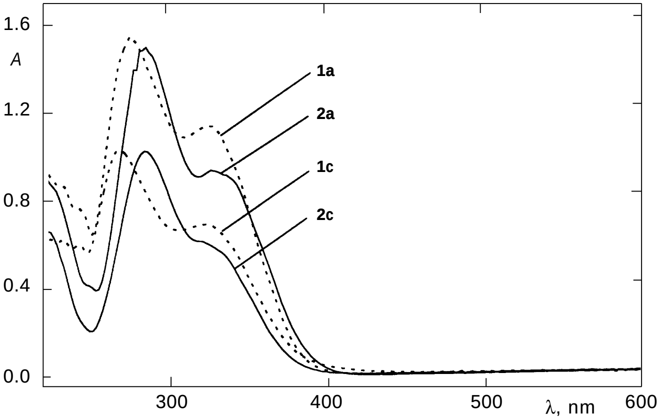


FIG. 3
UV-VIS spectra of **1a**, **2a**, **1c** and **2c**. THF, *l* = 0.1 cm, concentration 0.12 mg/ml (**1c**, **2c**), 0.15 mg/ml (**1a**, **2a**)

of triplet states by intersystem crossing from excited singlet states was observed in difference absorption spectra after excitation with a laser pulse (see Fig. 4, curve *3* for **1c**). These spectra have maxima at about 490 nm, the intensity of which decreases in the same order as fluorescence. The lifetime of the triplet states of all three compounds in air-saturated THF was 2.3 ± 0.3 μs. Difference absorption spectra of **1a** and other compounds are not measurable, changes in the absorbance after an excitation pulse are less than $2 \cdot 10^{-4}$. Changes in the molecular geometry between the ground state and the relaxed Franck–Condon excited state might be responsible for the large Stokes shift between the absorption and fluorescence band maxima of **1a**–**1d**. Another explanation can be based on the similarity of fluorescence and difference absorption spectra. We can assume that the excited triplet state of **1a**–**1d** is formed after excitation. Then, the green fluorescence corresponds with transition to the first triplet state. The detailed clarification of these processes is, however, beyond the frame of this contribution.

It was shown that both isomeric *N*-(4-substituted benzylidene)-4-ethynylanilines and 4-substituted *N*-(4-ethynylbenzylidene)anilines can be prepared and isolated as pure and stable compounds, applicable as monomers for new substituted polyacetylenes. Their reactivity in polymerization is expected to depend on electronic properties of acetylenic group. For example, it was suggested for rhodium-based catalysts, that the reactivity of monosubstituted acetylenes is controlled by the acidity of acetylenic

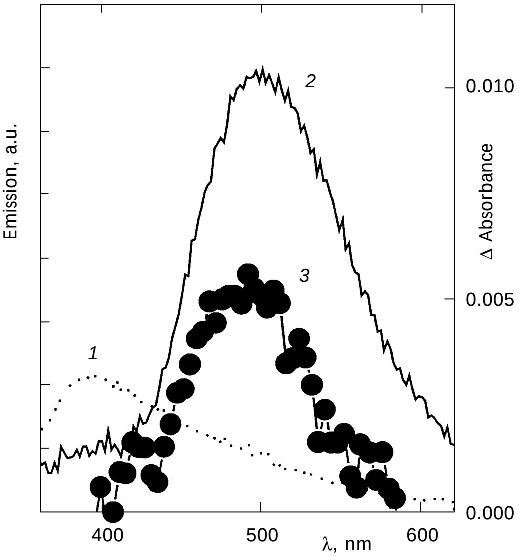


FIG. 4
Fluorescence spectra of **2c** (*1*) and **1c** (*2*) and difference absorption spectrum of **1c** 1 μs after excitation pulse (*3*). THF, concentration 0.06 mg/ml

hydrogen[19]. Actually, the reactivity of *N*-(4-substituted benzylidene)-4-ethynylanilines in the polymerization with rhodium cyclooctadiene complex as catalyst[3] was found to increase with increasing electronegativity of benzylidene ring substituents (and increasing acidity of acetylenic hydrogen) in the series: Me_2N < *t*-Bu < H < F < Br < NO_2. Isomeric 4-substituted *N*-(4-ethynylbenzylidene)anilines (**2a**–**2d**) were polymerized with the same catalyst[20]. In accord with higher acidity of acetylenic group, they exhibited higher reactivity providing polymers in higher yields and of higher molecular weights than the corresponding *N*-(4-substituted benzylidene)-4-ethynylanilines (**1a**–**1d**).

The possibility of tuning electronic properties of acetylenic group in monomers by varying substituents of aromatic rings may offer a chance to influence electronic density of the polyene backbone and the band gap energy of the corresponding polymers in a similar way. However, the data necessary for testing this possibility are not yet available. Moreover, the unique polymer properties such as electroconductivity and photoconductivity are known to depend on polymer microstructure, which is controlled rather by catalyst and polymerization conditions than by monomer.

The green fluorescence observed for some *N*-(4-substituted benzylidene)-4-ethynylanilines promises the possibility to get new fluorescent polyacetylene-type polymers as products of their polymerization. Preliminary experiments confirmed that polymers prepared by polymerization of **1a** and **1b** monomers exhibited fluorescence in the same region as monomers (for polymer THF solutions, broad band maxima were observed in the region 500–550 nm). The study of polyacetylenes prepared from aromatic Schiff bases described in this paper will continue.

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