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Near-infrared absorbing delocalized cationic azo dyes

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ABSTRACT

Novel, delocalized, cationic azo dyes derived from benzothiazole, benzoselenazole, indole and quinoline, displaying strong absorption around 700–800 nm, have been prepared in moderate to good yields. The synthesis involved the Knoevenagel condensation of an intermediate azo compound, possessing a 4-chloro-5-formylthiazole moiety, with methylenic bases generated *in situ* from benzoazolium and quinolinium salts.

1. Introduction

Near-infrared (NIR) absorbing dyes have been attracting increasing interest due to the rapid progress achieved in their high technology applications [1]. Despite the enormous synthetic versatility of azo dyes, which accounts for representing 50–70% of all commercially available dyes [2], little effort has been devoted to bring their absorption into the long wavelength region and only a few examples of NIR absorbing azo dyes have hitherto been disclosed [3–8]. The majority of the synthetic approaches make use of the known bathochromic effect of the thiazole ring [9], incorporated in the chromophoric system of the dye, to which the azo group is coupled to C-2 and a strong electron withdrawing conjugated moiety is linked to C-5. The use of a cationic heterocyclic residue as a powerful electron acceptor was first suggested by Griffiths, who reported the acid-catalyzed synthesis of the first two examples of a new class of NIR absorbing cationic azo dyes based on 4-chlorothiazole [7].

Recently we have described the synthesis of delocalized cationic azo dyes with absorption around 700 nm based on the Knoevenagel condensation of 2-(4-diethylaminophenylazo)thiazole-5-carbaldehyde with methylenic bases generated *in situ* from benzoazolium and quinolinium quaternary salts [8]. Following this strategy we envisioned that the absorption maxima of such dyes could be further pushed to the red end of the spectrum by the inclusion of a chlorine atom in the thiazole ring and/or by the use of a stronger electron donating amine as coupling component. The results of such study are disclosed herein.

2. Experimental

2.1. General

All reagents were of the highest purity available, purchased from Sigma–Aldrich Company, and were used as received. 2-Aminothiazole-5-carbaldehyde (**1**) [10], 2-amino-4-chlorothiazole-5-carbaldehyde (**2**) [11] and the quaternary ammonium salts **8** [12,13] were prepared according to the literature. Reactions were monitored by thin-layer chromatography using 0.25 mm aluminium-backed silica-gel plates (Merck 60 F_{254}). Melting points were measured in open capillary tubes in a Büchi 530 melting point apparatus and are uncorrected. IR spectra were recorded on a Mattson 5000 FTIR spectrophotometer. UV/vis spectra were performed on a Perkin–Elmer Lambda 6 instrument. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX 400 or ACP 250 spectrometers. Chemical shifts are reported with respect to the solvent or TMS as internal standard. Fast Atom Bombardment High Resolution mass spectra (FABHRMS) were determined on a Micromass AutoSpec M spectrometer, operating at 70 eV, using a matrix of 3-nitrobenzyl alcohol (3-NBA). Time-of-flight High Resolution mass

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spectrum (TOFHRMS) was determined on a Waters Micromass GCT spectrometer, operating in EI at 70 eV.

2.2. 4-Chloro-2-(4-diethylaminophenylazo)thiazole-5-carbaldehyde (**5**)

To 95–98% H_2SO_4 (5.6 mL) was added $NaNO_2$ (516 mg, 7.48 mmol) and the mixture was heated at 65 °C until complete dissolution. After being cooled in an ice-bath (0–5 °C), the nitrosylsulphuric acid solution was diluted with AcOH (3.2 mL) over 3 min and then left for 10 min. Following cooling to −5 °C, 2-amino-4-chlorothiazole-5-carbaldehyde (**2**) (1.0 g, 6.15 mmol) was added portion wise and, once the addition was complete (15 min.), the reaction mixture was stirred for 2 h at 5 °C. The so formed diazonium salt solution was added gradually (10 min.) to a solution of *N*,*N*-diethylaniline (1.0 mL, 6.29 mmol) in water (62 mL) and 95–98% H_2SO_4 (1.2 mL), at 0 °C under vigorous stirring, after which the reaction mixture was left at r.t. for 1 h. The resulting solid was then collected by filtration, washed with water and dried under reduced pressure over anhydrous P_2O_5 to afford **5**, which could be used subsequently without further purification. Yield: 87%. Dark-green crystals. M.p. 186 °C (dec.) (lit. 198–201 °C [14]). Vis (CH_2Cl_2) λ_{max} 570 nm. IR (KBr) ν_{max} 2985 (w), 2974 (w), 2929 (w), 2829 (w), 2707 (w), 1661 (m), 1603 (s), 1540 (w), 1484 (w), 1415 (m), 1310 (m), 1289 (m), 1272 (m), 1221 (s), 1128 (s), 1073 (m), 1006 (w), 876 (w), 715 (w) cm^{-1}. ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.29 (t, 6H, $J = 7.2$ Hz, CH_3), 3.54 (q, 4H, $J = 7.2$ Hz, CH_2), 6.78 (d, 2H, $J = 9.3$ Hz, Ar*H*), 7.94 (d, 2H, $J = 9.3$ Hz, Ar*H*), 10.03 (s, 1H, C*H*O). TOFHRMS: calc. for $C_{14}H_{15}N_4OS\,^{35}Cl$ $[M]^+$: 322.0655; found 322.0659; calc. for $C_{14}H_{15}N_4OS^{37}Cl$ $[M]^+$: 324.0626; found 324.0641.

2.3. 2-(2,3,6,7-Tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-ylazo)thiazole-5-carbaldehyde (**6**)

To a mixture of nitrosylsulphuric acid, prepared from 95–98% H_2SO_4 (3.0 mL) and $NaNO_2$ (270 mg, 3.91 mmol) as described above, and 98% H_3PO_4 (3.91 g), vigorously stirred at 0 °C, was slowly added (10 min) 2-aminothiazole-5-carbaldehyde (**1**) (0.5 g, 3.91 mmol). After 1 h the resulting diazonium salt solution was gradually added to a stirred mixture of julolidine (0.698 g, 3.91 mmol), sulphamic acid (190 mg) and 5% aqueous H_2SO_4 (38 mL) at 0 °C. Once the addition was complete (5 min.), the reaction mixture was stirred at 0 °C for 1 h and then poured onto water (100 mL) and extracted with AcOEt (3 × 100 mL). The combined organic layers were washed sequently with 1% aqueous $NaHCO_3$ (2 × 150 mL) and water (2 × 150 mL), dried over anhydrous $NaSO_4$ and the solvent removed under reduced pressure to afford chromatographically pure **6**. Yield: 28%. Blue crystals. M.p. 201 °C (dec.). Vis (CH_2Cl_2) λ_{max} 588 nm. IR (KBr) ν_{max} 3058 (w), 2919 (w), 2845 (w), 2790 (w), 2709 (w), 1662 (m), 1608 (m), 1537 (m), 1399 (w), 1305 (w), 1225 (s), 1200 (s), 1130 (s), 1075 (m), 984 (m), 909 (w), 866 (w), 656 (w), cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$) δ 1.99 (quintet, 4H, $J = 6.0$ Hz, NCH$_2$CH_2CH$_2$), 2.79 (t, 4H, $J = 6.0$ Hz, N(CH$_2$)$_2$CH_2), 3.39 (t, 4H, $J = 6.0$ Hz, NCH_2(CH$_2$)$_2$), 7.57 (s, 2H, Ar*H*), 8.39 (s, 1H, =C*H*N), 9.94 (s, 1H, C*H*O). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 21.1 (*C*H$_2$), 27.5 (*C*H$_2$), 29.7 (*C*H$_2$), 50.7 (*C*H$_2$), 121.8, 136.1, 142.5, 149.6, 152.3, 182.8, 184.8. FABHRMS (3-NBA) calc. for $C_{16}H_{17}N_4OS$ $[M + H]^+$: 313.1123; found 313.1120.

2.4. 4-Chloro-2-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]-quinolin-9-ylazo)thiazole-5-carbaldehyde (**7**)

Prepared from 2-amino-4-chlorothiazole-5-carbaldehyde (**2**) (0.5 g, 3.08 mmol) as described for the non-halogenated analogue **6**. Yield: 57%. Blue crystals. M.p. 197–199 °C. Vis (CH_2Cl_2) λ_{max} 612 nm. IR (KBr) ν_{max} 3105 (w), 2925 (m), 2853 (w), 2714 (w), 1651 (s), 1614 (s), 1536 (m), 1483 (w), 1403 (w), 1308 (s), 1293 (s), 1254 (s), 1231 (s), 1177 (s), 1144 (s), 1074 (m), 1026 (m), 985 (m), 913 (w), 803 (w) cm^{-1}; ^1H NMR (400.13 MHz, $CDCl_3$) δ 2.00 (quintet, 4H, $J = 6.1$ Hz, NCH$_2$CH_2CH$_2$), 2.78 (t, 4H, $J = 6.1$ Hz, N(CH$_2$)$_2$CH_2), 3.42 (t, 4H, $J = 6.1$ Hz, NCH_2(CH$_2$)$_2$), 7.55 (br s, 2H, Ar*H*), 9.99 (s, 1H, C*H*O). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 21.0 (*C*H$_2$), 27.4 (*C*H$_2$), 50.9 (*C*H$_2$), 127.4, 142.6, 147.3, 150.5, 182.0, 182.1. FABHRMS (3-NBA) calc. for $C_{26}H_{16}N_4OS\,^{35}Cl$ $[M + H]^+$: 347.0733; found 347.0734; calc. for $C_{26}H_{16}N_4OS\,^{37}Cl$ $[M + H]^+$: 349.0704; found 349.0701.

2.5. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-1-ethyl-3,3-dimethyl-3H-indolium iodide (**9a**)

A solution of the quaternary ammonium salt **8a** (1.0 mmol) and the intermediary azo dye **5** (1.0 mmol) in AcOH (5 mL) was heated at 40–45 °C for 28 h. The reaction mixture was then cooled to r.t., diluted with water (100 mL) and extracted repeatedly with Et_2O (4 × 100 mL). Potassium iodide (1.7 g, 10.0 mmol) was added to the remaining aqueous solution and the resulting precipitated dye was collected by filtration under reduced pressure. Drying under reduced pressure over anhydrous P_2O_5, followed by recrystallization from $CHCl_3/Et_2O$, afforded chromatographically pure **9a**. Yield: 74%. Dark solid. M.p. 177 °C (dec.). IR (KBr) ν_{max} 2975 (w), 1601 (m), 1571 (s), 1532 (m), 1409 (w), 1320 (w), 1304 (w), 1221 (s), 1203 (s), 1125 (s), 1112 (s), 1066 (s), 1004 (m), 929 (w), 872 (w), 715 (w) cm^{-1}. ^1H NMR (400.13 MHz, DMSO-d_6) δ 1.23 (t, 6H, $J = 7.0$ Hz, CH_3), 1.45 (t, 3H, $J = 7.1$ Hz, CH_3), 1.77 (s, 6H, C(CH_3)$_2$), 3.67 (q, 4H, $J = 7.0$ Hz, CH_2), 4.67 (q, 2H, $J = 7.1$ Hz, CH_2), 7.06 (d, 2H, $J = 9.4$ Hz, Ar*H*), 7.33 (d, 1H, $J = 15.7$ Hz, =C*H*C), 7.60–7.66 (m, 2H, Ar*H*), 7.86–7.93 (m, 4H, Ar*H*), 8.13 (d, 1H, $J = 15.7$ Hz, =C*H*C). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.7 (*C*H$_3$), 13.6 (*C*H$_3$), 26.1 (C*H*$_3$), 42.1 (*C*(CH$_3$)$_2$), 45.4 (*C*H$_2$), 51.9 (*C*H$_2$), 112.5, 115.0, 123.0, 125.9, 129.2, 129.3, 139.4, 140.5, 142.9, 143.6, 147.6, 154.6, 179.4, 180.0. FABHRMS (3-NBA) calc. for $C_{27}H_{31}N_5S\,^{35}Cl$ $[M]^+$: 492.1989; found 492.1981; calc. for $C_{27}H_{31}N_5S\,^{35}Cl$ $[M]^+$: 494.1959; found 494.1978.

2.6. Synthesis of dyes **9b–g** and **10a,b**: general procedure

A solution of the quaternary ammonium salt **8** (1.0 mmol) and the appropriated intermediary azo dye **5** or **6** (1.0 mmol) in EtOH (ca 15 mL) containing pyridine (1.5 mL) was stirred between r.t. and reflux until complete consumption of the starting azo dye. In each case, the temperature was carefully controlled to avoid the decomposition of both the starting material and the reaction product (**9b**: r.t., 5 h; 35 °C, 22 h. **9c**: r.t, 50 h. **9d**: r.t., 0.5 h; 35 °C, 26 h. **9e**: r.t., 0.5 h; 40 °C, 31 h. **9f**: r.t., 0.5 h; 40 °C, 0.5 h; reflux, 6 h. **9g**: r.t., 0.5 h; 35 °C, 0.5 h; reflux, 8.5 h. **10a**: r.t., 52 h. **10b**: r.t., 50 h). The reaction mixture was then cooled in an ice-bath and Et_2O was added. The resulting dark-blue solid was collected by filtration under reduced pressure, washed several times with Et_2O, redissolved in $CHCl_3$ and washed with water. The organic layer, after being separated by decantation, was dried over anhydrous $NaSO_4$ and evaporated to dryness. The resulting residue was purified by c.c. ($CHCl_3$/MeOH) (**9f**,**g**) or recrystallized from $CHCl_3/Et_2O$ (**9a–e**, **10b**) or MeOH/Et_2O (**10a**) until a chromatographically pure material was obtained (1–3 times).

2.6.1. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-3-ethylbenzothiazol-3-ium iodide (**9b**)

Yield: 72%. Dark solid. M.p. 192 °C (dec.). IR (KBr) ν_{max} 2975 (w), 1599 (m), 1576 (m), 1540 (w), 1461 (w), 1415 (w), 1310 (w), 1258 (m), 1233 (s), 1219 (s), 1130 (s), 1071 (m), 1006 (w), 756 (w) cm^{-1}. ^1H NMR (400.13 MHz, DMSO-d_6) δ 1.23 (t, 6H, $J = 7.0$ Hz, CH_3), 1.47 (t, 3H, $J = 7.2$ Hz, CH_3), 3.64 (q, 4H, $J = 7.0$ Hz, CH_2), 4.94 (q, 2H,

$J = 7.2$ Hz, CH_2), 7.02 (d, 2H, $J = 9.4$ Hz, Ar*H*), 7.75 (d, 1H, $J = 15.3$ Hz, =C*H*C), 7.78–7.90 (m, 4H, Ar*H*), 7.89 (d, 1H, $J = 15.3$ Hz, =C*H*C), 8.29 (d, 1H, $J = 8.4$ Hz, Ar*H*), 8.41 (d, 1H, $J = 7.9$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 13.2 (CH_3), 14.7 (CH_3), 45.1 (CH_2), 45.7 (CH_2), 113.9, 114.8, 117.2, 124.9, 126.3, 129.0, 129.0, 130.2, 135.9, 141.5, 143.0, 145.3, 154.7, 170.5, 179.1. FABHRMS (3-NBA) calc. for $C_{24}H_{25}N_5S_2$ ^{35}Cl $[M]^+$: 482.1240; found 482.1238; calc. for $C_{24}H_{25}N_5S_2$ ^{37}Cl $[M]^+$: 484.1210; found 484.1206.

2.6.2. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-3-hexylbenzothiazol-3-ium iodide (**9c**)

Yield: 54%. Dark solid. M.p. 150 °C (dec.). IR (KBr) ν_{max} 2927 (w), 1600 (m), 1575 (m), 1539 (w), 1461 (w), 1415 (w), 1308 (w), 1223 (s), 1164 (m), 1129 (s), 1070 (s), 1005 (w), 873 (w), 757 (w), 717 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 0.87 (t, 3H, $J = 6.9$ Hz, CH_3), 1.24 (t, 6H, $J = 7.0$ Hz, CH_3), 1.28–1.37 (m, 4H, CH_2), 1.40–1.46 (m, 2H, CH_2), 1.82–1.90 (m, 2H, CH_2), 3.64 (q, 4H, $J = 6.9$ Hz, CH_2), 4.90 (t, 2H, $J = 7.5$ Hz, CH_2), 7.02 (d, 2H, $J = 9.0$ Hz, Ar*H*), 7.72 (d, 1H, $J = 15.3$ Hz, =C*H*C), 7.80–7.98 (m, 4H, Ar*H*), 8.00 (d, 1H, $J = 15.3$ Hz, =C*H*C), 8.27 (d, 1H, $J = 8.1$ Hz, Ar*H*), 8.40 (d, 1H, $J = 9.0$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.4 (CH_3), 13.4 (CH_3), 21.6 (CH_2), 25.1 (CH_2), 28.4 (CH_2), 30.4 (CH_2), 45.0 (CH_2), 48.7 (CH_2), 113.6, 114.5, 116.6, 124.1, 125.5, 128.1, 128.3, 129.5, 135.1, 141.2, 142.3, 144.5, 154.0, 169.9, 178.3. FABHRMS (3-NBA) calc. for $C_{28}H_{33}N_5S_2$ ^{35}Cl $[M]^+$: 538.1866; found 538.1863; calc. for $C_{28}H_{33}N_5S_2$ ^{37}Cl $[M]^+$: 540.1836; found 540.1842.

2.6.3. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-3-ethyl-6-iodobenzothiazol-3-ium iodide (**9d**)

Yield: 66%. Dark solid. M.p. 195 °C (dec.). IR (KBr) ν_{max} 2976 (w), 1600 (m), 1585 (m), 1567 (w), 1451 (w), 1409 (w), 1333 (w), 1255 (w), 1216 (m), 1119 (s), 1070 (s), 1030 (w), 1006 (w), 873 (w), 716 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.22 (t, 6H, $J = 7.4$ Hz, CH_3), 1.45 (t, $J = 7.0$ Hz, 3H, CH_3), 3.64 (q, 4H, $J = 7.4$ Hz, CH_2), 4.89 (q, $J = 7.0$ Hz, 2H, CH_2), 7.02 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.68 (d, 1H, $J = 15.2$ Hz, =C*H*C), 7.83 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.99 (d, 1H, $J = 15.2$ Hz, =C*H*C), 8.06 (d, 1H, $J = 8.9$ Hz, Ar*H*), 8.17 (dd, 1H, $J = 1.5$, 8.9 Hz, Ar*H*), 8.82 (d, 1H, $J = 1.5$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.4 (CH_3), 14.8 (CH_3), 44.4 (CH_2), 45.0 (CH_2), 113.2, 113.6, 117.9, 125.5, 130.7, 132.1, 135.6, 137.9, 140.1, 142.4, 144.5, 154.0, 168.5 178.5. FABHRMS (3-NBA) calc. for $C_{24}H_{24}N_5S_2$ ^{35}ClI $[M]^+$: 608.0206; found 608.0199; calc. for $C_{24}H_{24}N_5S_2$ ^{37}ClI $[M]^+$: 610.0177; found 610.0189.

2.6.4. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-3-ethyl-benzoselenazol-3-ium iodide (**9e**)

Yield: 39%. Dark solid. M.p. 199 °C (dec.). IR (KBr) ν_{max} 2975 (w), 1600 (m), 1571 (m), 1538 (w), 1455 (w), 1330 (w), 1305 (w), 1251 (s), 1215 (s), 1129 (s), 1071 (m), 1006 (w), 873 (w), 759 (w), 716 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.21 (t, 6H, $J = 6.9$ Hz, CH_3), 1.43 (t, 3H, $J = 7.0$ Hz, CH_3), 3.61 (br s, 4H, CH_2), 4.92 (br s, 2H, CH_2), 6.98 (br s, 2H, Ar*H*), 7.70–7.72 (m, 2H, Ar*H*+, =C*H*C), 7.81–7.99 (m, 4H, =C*H*C + Ar*H*), 8.00–8.25 (m, 1H, Ar*H*), 8.45 (d, 1H, $J = 8.0$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.6 (CH_3), 14.1 (CH_3), 45.2 (CH_2), 45.4 (CH_2), 113.4, 117.1, 118.2, 126.2, 127.3, 128.1, 129.14, 130.6, 136.9, 142.1, 142.4, 144.7, 154.0, 178.3, 179.0. FABHRMS (3-NBA) calc. for $C_{24}H_{25}N_5S$ ^{35}Cl ^{78}Se $[M]^+$: 528.0692; found 528.0714; calc. for $C_{24}H_{25}N_5S$ ^{37}Cl ^{78}Se $[M]^+$: 530.0663; found 530.0684; calc. for $C_{24}H_{25}N_5S$ ^{35}Cl ^{80}Se $[M]^+$: 530.0684; found 530.0684; calc. for $C_{24}H_{25}N_5S$ ^{37}Cl ^{80}Se $[M]^+$: 532.0655; found 532.0683.

2.6.5. 2-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-1-ethylquinolinium iodide (**9f**)

Yield: 46%. Dark solid. M.p. 215 °C (dec.). IR (KBr) ν_{max} 2974 (w), 1600 (m), 1586 (m), 1538 (w), 1524 (w), 1411 (w), 1380 (w), 1304 (w), 1260 (m), 1218 (m), 1133 (s), 1071 (m), 1006 (w), 873 (w), 717 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.23 (t, 6H, $J = 7.0$ Hz, CH_3), 1.60 (t, 3H, $J = 7.1$ Hz, CH_3), 3.61 (q, 4H, $J = 7.0$ Hz, CH_2), 5.02 (q, 2H, $J = 7.1$ Hz, CH_2), 6.97 (d, 2H, $J = 8.9$ Hz, Ar*H*), 7.54 (d, 1H, $J = 15.3$ Hz, =C*H*C), 7.82 (d, 2H, $J = 8.9$ Hz, Ar*H*), 7.97 (t, 1H, $J = 7.5$ Hz, Ar*H*), 8.09 (d, 1H, $J = 15.3$ Hz, =C*H*C), 8.21 (t, 1H, $J = 7.9$ Hz, Ar*H*), 8.39 (d, 1H, $J = 8.2$ Hz, Ar*H*), 8.56 (d, 1H, $J = 8.9$ Hz, Ar*H*), 8.63 (d, 1H, $J = 8.9$ Hz, Ar*H*), 9.05 (d, 1H, $J = 8.9$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.4 (CH_3), 13.8 (CH_3), 44.7 (CH_2), 46.6 (CH_2), 112.8, 118.6, 120.3, 121.4, 126.6, 128.2, 128.9, 130.1, 134.0, 135.1, 137.9, 141.9 142.6, 144.2, 153.5, 177.0. FABHRMS (3-NBA) calc. for $C_{26}H_{27}N_5S$ ^{35}Cl $[M]^+$: 476.1676; found 476.1668; calc. for $C_{26}H_{37}N_5S$ ^{37}Cl $[M]^+$: 478.1646; found 478.1662.

2.6.6. 4-{2-[4-Chloro-2-(4-diethylaminophenylazo)thiazol-5-yl]-vinyl}-1-ethylquinolinium iodide (**9g**)

Yield: 40%. Dark solid. M.p. 186 °C (dec.). IR (KBr) ν_{max} 2970 (w), 1604 (m), 1584 (m), 1563 (m), 1540 (w), 1480 (w), 1310 (w), 1246 (m), 1195 (m), 1141 (s), 1071 (m), 1002 (w), 873 (w), 717 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.21 (t, 6H, $J = 7.0$ Hz, CH_3), 1.59 (t, 3H, $J = 7.0$ Hz, CH_3), 3.60 (q, 4H, $J = 7.0$ Hz, CH_2), 5.02 (q, 2H, $J = 7.0$ Hz, CH_2), 6.98 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.80 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.99–8.04 (m, 3H, Ar*H*+, =C*H*C), 8.24 (t, 1H, $J = 8.3$ Hz, Ar*H*), 8.55 (d, 1H, $J = 9.0$ Hz, =C*H*C), 8.62 (d, 1H, $J = 6.5$ Hz, Ar*H*), 8.97 (d, 1H, $J = 8.5$ Hz, Ar*H*), 9.38 (d, 1H, $J = 6.5$ Hz, Ar*H*). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 12.6 (CH_3), 15.1 (CH_3), 44.9 (CH_2), 52.2 (CH_2), 112.8, 117.2, 119.0, 123.0, 126.5, 126.7, 127.8, 129.3, 130.0, 135.1, 137.5, 141.5, 141.9, 147.2, 151.0, 153.4, 176.4. FABHRMS (3-NBA) calc. for $C_{26}H_{27}N_5S$ ^{35}Cl $[M]^+$: 476.1676; found 476.1660; calc. for $C_{26}H_{27}N_5S$ ^{37}Cl $[M]^+$: 478.1646; found 478.1658.

2.6.7. 1-Ethyl-3,3-dimethyl-2-{2-[2-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-ylazo)thiazol-5-yl]vinyl}-3H-indolium (**10a**)

Yield: 22%. Dark solid. M.p. 200 °C (dec.). IR (KBr) ν_{max} 3033 (w), 2966 (w), 1563 (m), 1530 (m), 1461 (w), 1430 (w), 1402 (w), 1327 (w), 1262 (m), 1226 (m), 1185 (s), 1153 (s), 1114 (s), 1073 (s), 1023 (m), 978 (m), 897 (w), 778 (w), 763 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.41 (t, 3H, $J = 7.1$ Hz, CH_3), 1.78 (s, 6H, C(CH_3)$_2$), 1.93 (br quintet, 4H, NCH$_2$C*H*$_2$CH$_2$), 2.79 (br t, 4H, N(CH$_2$)$_2$C*H*$_2$), 3.53 (br t, 4H, NC*H*$_2$(CH$_2$)$_2$), 4.60 (q, 2H, $J = 7.1$ Hz, CH_2), 7.10 (d, 1H, $J = 15.4$ Hz, =C*H*C), 7.46 (br s, 2H, Ar*H*), 7.57–7.60 (m, 2H, Ar*H*), 7.85 (d, 2H, $J = 7.6$ Hz, Ar*H*), 8.66 (d, 1H, $J = 15.4$ Hz, =C*H*C), 8.72 (s, 1H, =C*H*N). ^{13}C NMR (100.61 MHz, DMSO-d_6) δ 13.4 (CH_3), 20.2 (CH_3), 25.7 (CH_2), 26.6 (CH_2), 41.4 (C(CH_3)$_2$), 50.6 (CH_2), 51.6 (CH_2), 110.3, 114.4, 122.9, 128.6, 129.0, 133.1, 140.5, 142.7, 143.4, 144.1, 150.9, 155.9, 179.3, 183.9. FABHRMS (3-NBA) calc. for $C_{29}H_{32}N_5S$ $[M]^+$: 482.2378; found 482.2357.

2.6.8. 3-Ethyl-2-{2-[2-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]-quinolin-9-ylazo)thiazol-5-yl]vinyl}benzothiazol-3-ium (**10b**)

Yield: 22%. Dark solid. M.p. 184 °C (dec.). IR (KBr) ν_{max} 2921 (w), 2850 (w), 1608 (w), 1594 (w), 1578 (w), 1536 (w), 1252 (m), 1203 (m), 1227 (m), 1129 (s), 1075 (m), 1026 (w), 980 (w), 919 (w), 828 (w), 693 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ 1.44 (t, 3H, $J = 7.1$ Hz, CH_3), 1.91 (br quintet, 4H, NCH$_2$C*H*$_2$CH$_2$), 2.74 (br t, 4H, N(CH$_2$)$_2$C*H*$_2$), 3.40 (br t, 4H, NC*H*$_2$(CH$_2$)$_2$), 4.87 (q, 2H, $J = 7.1$ Hz, CH_2), 7.38 (br s, 2H, Ar*H*), 7.54 (d, 1H, $J = 15.2$ Hz, =C*H*C), 7.75 (t, 1H, $J = 8.1$ Hz, Ar*H*), 7.84 (t, 1H, $J = 8.1$ Hz, Ar*H*), 8.23 (d, 1H, $J = 8.1$ Hz, Ar*H*), 8.36–8.40 (m, 2H, =C*H*C + Ar*H*), 8.47 (s, 1H, =C*H*N). ^{13}C NMR (100.61 MHz, DMSO-d_6): δ 14.1 (CH_3), 20.2 (CH_3), 26.7 (CH_2), 44.1 (CH_2), 50.3 (CH_2), 111.9, 116.2, 124.3, 128.0, 128.1, 129.4, 132.4, 139.4, 140.8, 142.0, 150.0, 152.5, 170.1, 182.4. FABHRMS (3-NBA) calc. for $C_{26}H_{26}N_5S_2$ $[M]^+$: 472.1630; found 472.1628.

3. Results and discussion

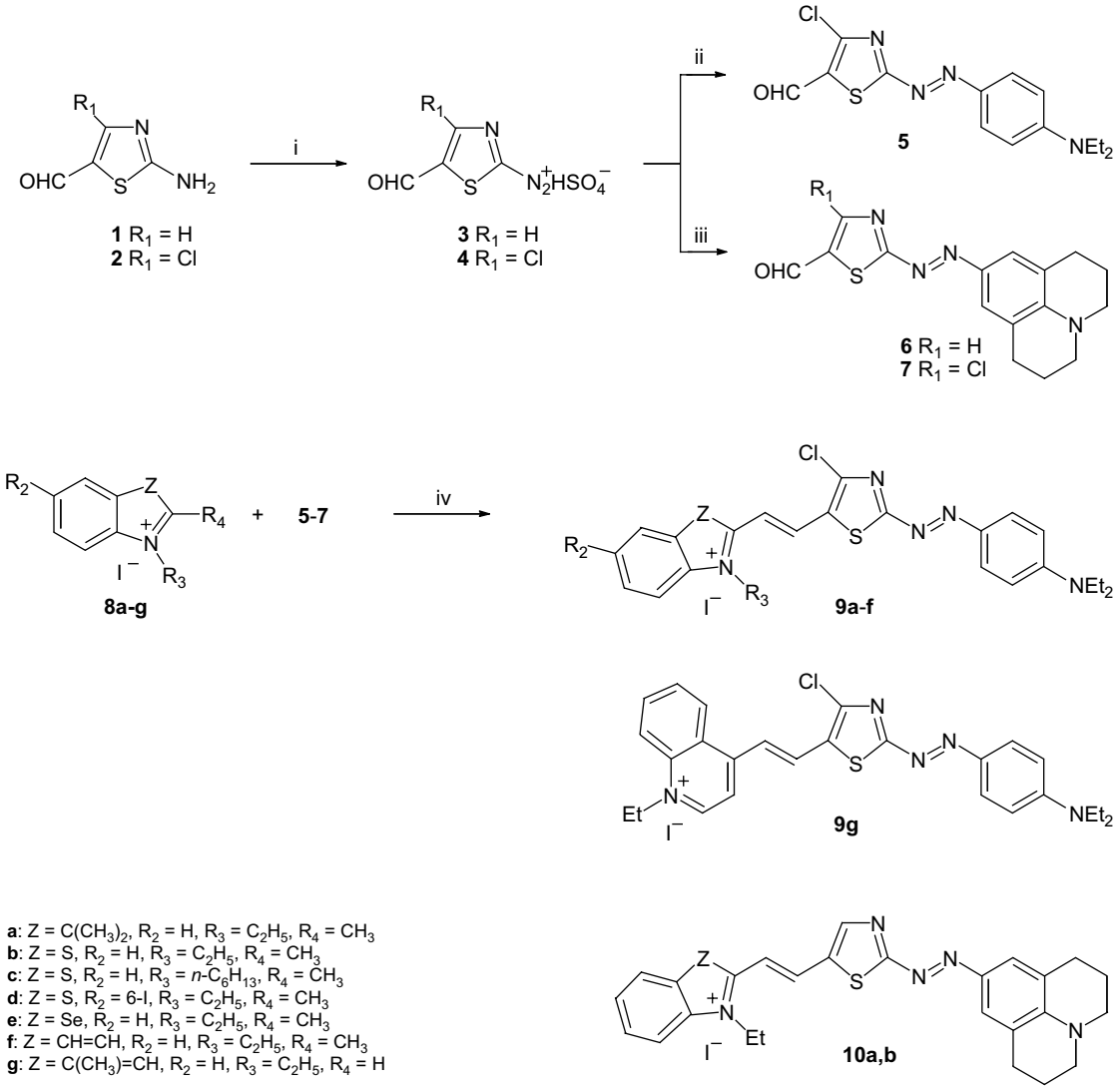
To assess the bathochromic influence of the chlorine atom, several delocalized cationic azo dyes **9** were synthesized by the Knoevenagel condensation of 4-chloro-2-(4-diethylaminophenylazo)thiazole-5-carbaldehyde (**5**) with themethylenic bases generated from benzoazolium and quinolinium salts **8a–g** in EtOH/pyridine. The starting aldehyde **5** was prepared from the readily accessible 2-amino-4-chlorothiazole-5-carbaldehyde (**2**), by diazotation with nitrosylsulphuric acid, followed by coupling with *N*,*N*-diethylaniline (Scheme 1).

Dyes **9** were obtained in moderate to good yields, except in case of compound **9a** for which only vestiges were isolated. The use of different basic conditions was unsuccessful in improving its yield, which finally could be raised to 74% carrying out the condensation in AcOH. For all the other dyes similar acid-catalyzed conditions invariably provided either very complex reaction mixtures or the desired compound in very low yield.

As expected, the introduction of the chlorine atom into the 4-position of the thiazole ring produces a bathochromic shift in the absorption spectrum of the dyes in relation to the parent non-halogenated compounds [8]. For the intermediate formyl dyes **5** and **7** the red shift was, in CH_2Cl_2, 21 and 24 nm, respectively, while for cationic dyes **9a–g** it ranged consistently from 18 to 24 nm in the same solvent (Table 1).

Despite their similarity to polymethine dyes, compounds **9a–g** display wavelengths of maximum absorption which depend neither from the basicity of the heteroaromatic nuclei nor from the length of the π-conjugated system, as those of polymethine dyes do (indole < benzothiazole < benzoselenazole < quinoline < lepidine) [15]. This same behaviour was previously observed for the non-halogenated analogues of dyes **9**. In this respect it is noticeable that the most bathochromic dye, **9a**, is derived precisely from the poorer heteroaromatic electron acceptor, while the quinoline-based dye **9f** displays a value of λ_{max} superior to that of the lepidine-derived dye **9g**, although the latter possesses a more extended chromophore. Not surprisingly, the influence of the length of the *N*-alkyl chain on the λ_{max} of the dyes seems to be insignificant as illustrated for dyes **9b** and **9c** possessing, respectively, and a *N*-ethyl and *N*-hexyl pendent group.

In order to further increase the maximum absorption of the dyes we attempted to synthesise analogues of **9** derived from known strong electron donating coupling components in azo dyes, namely, 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (julolidine) [16],



Scheme 1. Reagents and conditions. (i) **3**: H_2SO_4, $NaNO_2$, AcOH, −5 to 5 °C; **4**: H_2SO_4, $NaNO_2$, H_3PO_4, 0 °C; (ii) *N*,*N*-diethylaniline, H_2SO_4, H_2O, 0 °C → r.t.; (iii) julolidine, NH_2SO_3H, H_2SO_4, H_2O, 0 °C; (iv) **9a**: AcOH, 40–45 °C; **9b–g**, **10a**,**b**: EtOH, pyridine, r.t.-reflux.

Table 1
Vis spectral data of azo dyes **9** and **10** in various solvents.[a]

Dyes	λ_{max} (nm)						ε_{max}
	$CHCl_3$	Cyclopentanone	CH_2Cl_2	Acetone	DMSO	MeOH	CH_2Cl_2
9a	726	705	747	690	699	693	771,00
9b	000	657	708	648	660	651	826,00
9c	679	666	711	657	666	654	73,000
9d	000	672	732	663	669	663	62,700
9e	000	663	717	657	663	654	57,600
9f	000	639	678	624	642	624	43,800
9g	000	636	672	618	633	621	45,200
10a	000	744	810	732	741	729	105,400
10b	000	696	756	684	690	684	60,500

[a] Empirical parameters of solvent polarity E_T (30) (kcal mol^{-1}) [19]: $CHCl_3$ 39.1, cyclopentanone 39.4, CH_2Cl_2 40.7, acetone 42.2, DMSO 45.1, MeOH 55.4.

5-acetylamino-2-methoxy-*N*,*N*-diethylaniline [17] and 2,2-dimethyl-2,3-dihydro-1*H*-perimidine [18]. However, despite the number of different reaction conditions employed in either diazotation or coupling steps, the isolated material was generally in quantity and/or purity unsuitable to carry on with the subsequent Knoevenagel condensation. Only julolidine provided the intermediary azo compounds **6** and **7** in 28 and 57% yield, respectively. The former could be condensed with 2,3,3-trimethylindolenium (**8a**) and 2-methylbenzothiazolium (**8b**) iodides to afford the correspondent delocalized azo dyes **10a** and **10b**.

Both delocalized cationic azo dyes **10** display a significant bathochromic shift in relation to the parent *N*,*N*-diethylamino derivatives (64 and 81 nm, respectively).

In the ^{1}H NMR spectra of compounds **9** and **10** the protons of the exocyclic C–C double bond present coupling constants around 15 Hz, typical of *trans* geometry. An exception is the lepidine-based dye **9g** whose olefinic protons exhibit a vicinal coupling constant of 9.0 Hz. Since a *cis* configuration seems to be unlikely, given the inherent strong steric hindrance, the observed low value of *J* probably arises from a dihedral angle between the two C–H bonds somewhat inferior to 180°. This lack of planarity and the consequent diminishing of orbital overlapping should be responsible, at least partially, for **9g** displaying λ_{max} inferior to that of the less conjugated quinoline-based dye **9f**, whatever the solvent.

The condensation of **7**, that would lead to dyes bearing simultaneously a chlorine atom and a julolidine moiety in the chromophoric system, invariably resulted in very complex mixtures either under basic (EtOH, pyridine, r.t.-reflux) or acid catalysis (AcOH, 45 °C).

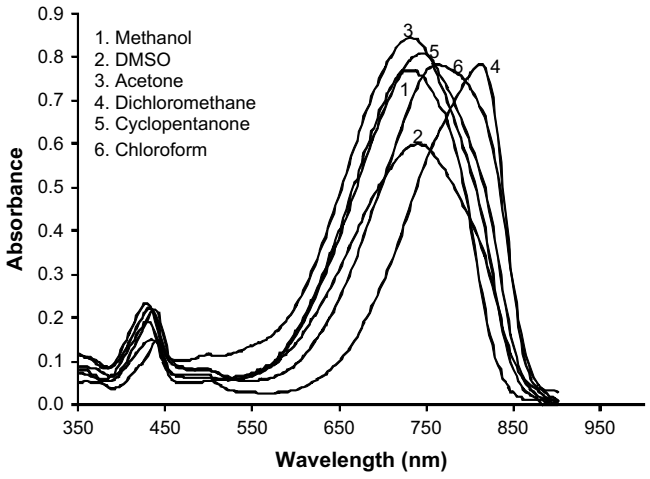


Fig. 1. Absorption spectra of dye **10a** in various solvents.

In order to investigate the solvatochromic behaviour of the synthesized dyes their absorption spectra were performed in a variety of organic solvents (Table 1). The λ_{max} of the dyes was found to exhibit a strong solvent dependency, which, however, did not show a regular variation with the polarity of the solvents. Despite the general trend seems to point to an increase of bathochromicity with increasing solvent polarity, genuine negative solvatochromism cannot be securely ascribed since a complete study of the absorption in solvents of low polarity was hampered by the low solubility of the dyes. Besides, frequently hetarylazo azo dyes are more bathochromic in solvents of intermediate polarity and more hypsochromic in solvents of lower and higher polarities [20–22].

In general, it was observed that the absorption spectra of the dyes in MeOH, DMSO and acetone did not differ very significantly. The higher values of λ_{max} were obtained in CH_2Cl_2 and the largest observed shifts of λ_{max} were from CH_2Cl_2 to MeOH. They ranged from 51 to 81 nm, being more pronounced for the 6-iodobenzothiazolium dye **10a** (Fig. 1).

4. Conclusions

We have synthesized and characterized several new NIR absorbing delocalized cationic azo dyes, a rarely explored class of azo dyes. The key step of the synthesis is the Knoevenagel condensation of an intermediate azo compound possessing a 5-formylthiazole moiety with methylenic bases generated *in situ* from benzoazolium and quinolinium salts.

All the delocalized azo dyes synthesized have shown solvatochromic behaviour.

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