Synthesis and properties of merocyanine dyes derived from *N*-aryl-substituted pyridinium salts and cyanoacetic acids

I. A. Borisova, * A. A. Zubarev, L. A. Rodinovskaya, and A. M. Shestopalov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. E-mail: irdbor@gmail.com

A series of merocyanine dyes were synthesized by two-component condensation of *N*-aryl-4-picolinium salts and cyanoacetic acid derivatives. Physicochemical properties of the synthesized dyes were studied.

Key words: 4-picolinium salts, heterocycles, merocyanine dyes, spectral properties, protonation.

One of the key fundamental directions of the organic chemistry is the design of new compounds with desired properties that are capable of undergoing transformations with the changes of the conditions (temperature, electric current, light, pH, *etc.*).¹ Among such compounds are merocyanine dyes, the systems bearing simultaneously donor and acceptor moieties linked with the polymethine chain.^{2,3} As a rule, the donor fragments of the known merocyanines are heterocycles, *e.g.*, indoles, benzothi-azoles, and benzoxazoles.^{2,4–11} Examples of merocyanines comprising more basic heterocycles, for instance, pyridine and quinoline, are scarce.^{12–19}

It was assumed, that merocyanine dyes bearing the dihydropyridine moiety are prospective for use in optoelectronic devices, photovoltaic applications, laser filters, and photodynamic therapy.^{20,21}

Earlier, we have developed synthesis of merocyanine dyes from *N*-alkyl-substituted azinium salts and cyano-acetic acid derivatives.¹² To date, only Bespalov and co-workers²² published the synthesis of merocyanine systems bearing *N*-aryl-substituted dihydropyridine cycles. It should be noted that merocyanines have been synthesized²² via modification of the γ -pyrone donor fragment with amines and the ring-closed methine chain linking donor and acceptor fragments was a structural part of bis(dicyanomethylene)indane.

Therefore, the aim of the present work is to develop a simple and versatile procedure to access merocyanine dyes from *N*-aryl-substituted 4-picolinium salts and cyanoacetic acid derivatives. The studies of physicochemical properties of the synthesized dyes will allow uncovering structure—property relationship.

Results and Discussion

In the present work, merocyanine dyes **9a-h** (Scheme 1) were synthesized by base-mediated two-component con-

densation of ethoxymethylidene derivatives of CH acids 7 and 8 with γ -picolinium salts 2–6. The starting salts 2–6 were obtained from γ -picoline 1 as earlier described.²³

Synthesis of merocyanines 9a-h revealed that the acceptor substituents on the aromatic ring either lowered the yields of the target dyes (synthesis of compounds 9g,h from salt 2), or completely suppress the reaction (synthesis of merocyanine dyes from salt 6 failed). Salts 3-5 bearing the donor substituents on the aryl group gives dyes 9a-f in good yields (42–62%). Note that the yields of the target dyes decrease as the donor ability of the substituent on the aromatic ring increases.

We recorded the UV spectra of the synthesized dyes (Fig. 1). It was found that the absorption maxima of the studied compounds **9a**—**h** are at about 500 nm. It follows from Fig. 1 that the absorption maxima of merocyanine dyes **9a**—**h** are shifted slightly to the long wavelength range with increasing donor ability of the substituents on the aromatic ring. The replacement of the donor substituent with the acceptor one (compounds **9g,h**) results in the opposite changes in the UV spectra, *i.e.*, the absorption maximum is shifted towards shorter wavelengths. Analysis of the UV spectra of merocyanines **9a**—**h** reveals that intensity of the absorption maximum noticeably decreases when the acceptor substituent with two cyano groups is replaced with the acceptor with one CN.

Solvatochromic properties of the synthesized dyes were studied using compound **9a** as a model (Fig. 2). It follows from Fig. 2 that an increase in the solvent polarity (relative to medium polar dichloromethane) leads to a hypsochromic shift of the absorption maximum. A decrease in the solvent polarity (benzene is used as a solvent) results in the broadening of the absorption maximum and its shift to the long wavelength range.

Protonation of merocyanine **9a** with trifluoroacetic acid occurs at the γ position of the polymethine chain and is accompanied with decolorization of its solution (Scheme 2).

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 1868-1872, October, 2018.

1066-5285/18/6710-1868 © 2018 Springer Science+Business Media, Inc.



3 (75%), **4** (53%), **5** (47%), **6** (92%)

R = H (3), Me (4), OMe (5), Cl (6)



R³ = CN (**7**), COOEt (**8**)

Com- pound 9	R ¹	R ²	R ³	Yield (%)	Com- pound 9	R ¹	R ²	R ³	Yield (%)
a	Н	Н	CN	50	e	OMe	Н	CN	42
b	Н	Н	COOEt	62	f	OMe	Н	COOEt	44
с	Me	Н	CN	63	g	NO_2	NO_2	CN	30
d	Me	Н	COOEt	62	ĥ	NO ₂	NO ₂	COOEt	38

This direction of the protonation of dye 9a is confirmed by the presence of the doublet at δ 4.5 and a low-field shift of the heterocyclic proton signals in the ¹H NMR spectrum (Fig. 3). UV spectrum of the protonated dye 9a lacks the absorption at 504 nm. This is indicative of the disruption of the conjugation between the heterocyclic moiety and the side chain (Fig. 4).





In the IR spectra of dyes 9a,c,e,g bearing the acceptor cyano groups, the absorption bands of the CN groups are shifted to the 2200–2190 cm⁻¹ range as compared to benzylidenemalononitrile²⁴ showing the CN absorption bands in the 2220 cm⁻¹ range. Since two cyano groups of dyes 9a,c,e,g are nonequivalent, two IR absorption bands at 2200 and 2190 cm⁻¹ are observed thus evidencing the greater involvement of one of the CN groups in conjugation.

The absorption bands of the CN groups of dyes 9b,d,f,hbearing the acceptor ethyl cyanoacetate moiety are also appeared in the 2190 cm⁻¹ range and their ester groups absorb at about 1660 cm⁻¹. The signal of the CO₂Et group is significantly shifted relative to the same signal of the reference compound,²⁵ consequently, the CO₂Et group generally contributes to the negative charge delocalization over the dye molecule.

In summary, we synthesized new merocyanine dyes **9a**—**h** bearing the aryl substituents on the nitrogen atom of 1,4-dihydropyridine moiety. The absorption maxima of



Fig. 1. UV spectra of compounds 9a-h (CH₂Cl₂, $C_M = 1 \cdot 10^{-5} \text{ mol } L^{-1}$).



Fig. 2. UV spectra of compounds **9a** recorded in acetonitrile (1), acetone (2), dichloromethane (3), DMSO (4), ethanol (5), and benzene (6) ($C_{\rm M} = 1 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$).

the synthesized dyes appear at the long wavelength range (500 nm). Using dye 9a as a model, it was shown that dyes derived from *N*-aryl-substituted pyridinium salts and cyanoacetic acid derivatives exhibit a small negative solvatochromism. It was found that protonation of com-



Fig. 3. ¹H NMR spectra of unprotonated (*a*) and protonated (*b*) forms of compound **9a**. Spectrum of unprotonated form was recorded in DMSO-d₆, spectrum of protonated form, in CF₃COOH.



Fig. 4. UV spectra of unprotonated (1) and protonated (2) forms of compound 9a (CH₂Cl₂, $C_{\rm M} = 1 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$).

pound **9a** results in disruption of the π,π conjugation between the heterocyclic fragment and the side chain; therefore, the protonation occurs at the C(γ) atom of the polymethine chain.

Experimental

¹H and ¹³C NMR spectra were run on a Bruker AM300 spectrometer in DMSO-d₆. IR spectra were recorded with a Bruker ALPHA-T spectrometer in KBr pellets. UV spectra were obtained on an Agilent 8453 UV-visible spectrophotometer

equipped with the 1-cm path length quartz cell in CH₂Cl₂ at a concentration of the studied compounds of $C_{\rm M} = 1 \cdot 10^{-5}$ mol L⁻¹. High resolution mass spectrometry was performed with a micrOTOF instrument. All solvents were purified by standard procedures prior to use. The reaction courses were monitored by TLC on Merck plates; the spots were visualized using iodine vapors or UV light ($\lambda = 254$ nm). Salts **2–6** were synthesized by known procedure.²³

Synthesis of merocyanine dyes 9a—h (general procedure). To a solution of the starting salts 2—6 (1.0 mmol) in DMF (3 mL), triethylamine (279 μ L, 2.0 mmol) was added dropwise followed by addition of CH acid derivative 7, 8 (2.0 mmol). The stirred mixture was heated at 70 °C for 3 h, cooled down, diluted with water, the precipitate formed was collected by filtration, washed successively with aqueous HCl (pH 4) and water, and air dried.

2-(2-[1-Phenylpyridin-4(1*H***)-ylidene]ethylidene)malononitrile (9a).** Yield 123 mg (50%), orange crystals, m.p. 250–252 °C. IR, v/cm⁻¹: 2190 (=C=N), 2206 (CN). UV (CH₂Cl₂), λ_{max}/nm (lgɛ): 504 (4.43). ¹H NMR, δ : 5.81 (d, 1 H, C(3)H, *J* = 13.9 Hz); 7.05 (br.s, 1 H, CH_{pyr}); 7.45–7.81 (m, 5 H, 5 CH_{Ar}); 8.00 (d, 1 H, C(2)H, *J* = 13.9 Hz); 8.12–8.25 (m, 3 H, 3 CH_{pyr}). ¹³C NMR, δ : 103.43, 114.63, 119.10, 120.59, 123.34, 129.31, 130.47, 138.69, 139.64, 142.64, 150.13, 152.14. MS, found: *m/z* 246.1038 [M + H]⁺. C₁₆H₁₁N₃. Calculated: [M + H] = 246.1026.

Ethyl 2-cyano-4-(1-phenylpyridin-4(1*H*)-ylidene)but-2-enoate (9b). Yield 181 mg (62%), burgundy crystals, m.p. 200–202 °C. IR, ν /cm⁻¹: 2187 (CN), 1671 (C=O). UV (CH₂Cl₂), λ_{max} /nm (lgc): 508 (4.47). ¹H NMR, δ : 1.21 (t, 3 H, CO₂CH₂CH₃, *J* = 7.1 Hz); 4.11 (q, 2 H, CO₂CH₂CH₃, *J* = 7.1 Hz); 5.74 (s, 1 H, C(3)H); 6.98 (br.s, 1 H, CH_{pyr}); 7.30–7.77 (m, 6 H, 5 CH_{Ar} and CH_{pyr}); 7.99–8.20 (m, 3 H, 2 CH_{pyr} and C(2)H). ¹³C NMR, δ : 15.01, 59.81, 102.75, 113.73, 118.96, 119.83, 123.08, 129.07, 130.50, 138.16, 138.84, 142.67, 147.81, 152.15. MS, found: *m*/*z* 293.1273 [M + H]⁺. C₁₈H₁₆N₂O₂. Calculated: [M + H] = 293.1285.

2-(2-[1-{*p***-Tolyl}pyridin-4(1***H***)-ylidene]ethylidene)malononitrile (9c). Yield 163 mg (63%), orange crystals, m.p. 243–245 °C. IR, v/cm⁻¹: 2191 (=C=N), 2208 (CN). UV (CH₂Cl₂), \lambda_{max}/nm (lgɛ): 505 (4.21). ¹H NMR, δ: 2.38 (s, 3 H, CH₃); 5.80 (d, 1 H, C(3)H,** *J* **= 14.1 Hz); 7.10 (br.s, 1 H, CH_{pyr}); 7.37–7.62 (m, 5 H, 4 CH_{Ar} and CH_{pyr}); 7.97 (d, 1 H, C(2)H,** *J* **= 14.1 Hz); 8.14 (d, 2 H, 2 CH_{pyr},** *J* **= 7.4 Hz). ¹³C NMR, δ: 20.95, 103.35, 114.64, 118.57, 120.68, 123.12, 130.82, 138.67, 139.11, 140.36, 149.92, 152.40. MS, found:** *m***/***z* **260.1181 [M + H]⁺. C₁₇H₁₃N₃. Calculated: [M + H] = 260.1182.**

Ethyl 2-cyano-4-(1-[*p***-tolyl]pyridin-4(1***H***)-ylidene)but-2-enoate (9d). Yield 190 mg (62%), crimson crystals, m.p. 204–206 °C. IR, v/cm⁻¹: 2188 (CN), 1674 (C=O). UV (CH₂Cl₂), \lambda_{max}/nm (lgɛ): 507 (4.52). ¹H NMR, δ: 1.21 (t, 3 H, CO₂CH₂CH₃, J = 7.1 Hz); 2.38 (s, 3 H, CH₃); 4.10 (q, 2 H, CO₂CH₂CH₃, J = 7.1 Hz); 5.77 (d, 1 H, C(3)H, J = 14.2 Hz); 6.98 (br.s, 1 H, CH_{pyr}); 7.39 (d, 2 H, 2 CH_{Ar}, J = 8.5 Hz); 7.52 (d, 2 H, 2 CH_{Ar}, J = 8.5 Hz); 8.01–8.12 (m, 4 H, 3 CH_{pyr} and C(2)H). ¹³C NMR, δ: 15.02, 20.94, 59.76, 102.65, 113.69, 118.93, 119.91, 122.88, 130.85, 138.21, 138.85, 140.39, 147.45, 152.16, 166.10. MS, found: m/z 307.1437 [M + H]⁺. C₁₉H₁₈N₂O₂. Calculated: [M + H] = = 307.1441.**

2-(2-[1-{4-Methoxyphenyl}pyridin-4(1*H***)-ylidene]ethylidene)malononitrile (9e). Yield 116 mg (42%), red crystals, m.p. > > 260 °C. IR, v/cm⁻¹: 2185 (=C=N), 2206 (CN). UV (CH₂Cl₂), \lambda_{max}/nm (lgɛ): 503 (4.47). ¹H NMR, δ: 3.83 (s, 3 H, OCH₃);** 5.79 (d, 1 H, C(3)H, J = 14.2 Hz); 7.01–7.12 (m, 3 H, 2 CH_{Ar} and CH_{pyr}); 7.59 (m, 3 H, 2 CH_{Ar} and CH_{pyr}); 7.95 (d, 1 H, C(2)H, J = 14.2 Hz); 8.12 (d, 2 H, CH_{pyr}, J = 7.1 Hz). ¹³C NMR, δ : 56.16, 103.23, 115.47, 118.70, 120.81, 124.85, 135.94, 138.99, 139.45, 139.90, 149.66, 152.33, 159.92. MS, found: m/z 276.1140 [M + H]⁺. C₁₇H₁₃N₃O. Calculated: [M + H] = 276.1131.

Ethyl 2-cyano-4-(1-[4-methoxyphenyl]pyridin-4(1*H***)-ylidene)but-2-enoate (9f). Yield 142 mg (44%), crimson crystals, m.p. 191–193 °C. IR, v/cm⁻¹: 2187 (CN), 1665 (C=O). UV (CH₂Cl₂), \lambda_{max}/nm (lgε): 508 (4.46). ¹H NMR, δ: 1.21 (t, 3 H, CO₂CH₂CH₃,** *J* **= 7.1 Hz); 3.82 (s, 3 H, OCH₃); 4.10 (q, 2 H, CO₂CH₂CH₃,** *J* **= 7.1 Hz); 5.76 (d, 1 H, C(3)H,** *J* **= 14.2 Hz); 6.97 (br.s, 1 H, CH_{pyr}); 7.12 (d, 2 H, 2 CH_{Ar},** *J* **= 9.0 Hz); 7.36 (br.s, 1 H, CH_{pyr}); 7.56 (d, 2 H, 2 CH_{Ar},** *J* **= 9.0 Hz); 7.98–8.11 (m, 3 H, C(2)H and 2 CH_{pyr}). ¹³C NMR, δ: 15.04, 56.13, 59.70, 102.50, 115.50, 118.94, 120.04, 124.63, 135.98, 138.63, 139.25, 147.21, 152.16, 159.76, 166.17. MS, found:** *m/z* **323.1395 [M + H]⁺. C₁₉H₁₈N₂O₃. Calculated: [M + H] = 323.1390.**

2-(2-[1-{2,4-Dinitrophenyl}pyridin-4(1*H***)-ylidene]ethylidene)malononitrile (9g). Yield 101 mg (30%), dark violet crystals, m.p. 242–244 °C. IR, v/cm⁻¹: 2202 (CN). UV (CH₂Cl₂), \lambda_{max}/nm (lg₆): 472 (4.37), 500 (4.37). ¹H NMR, \delta: 5.87 (d, 1 H, C(3)H,** *J* **= 13.5 Hz); 6.99 (d, 1 H, CH_{pyr},** *J* **= 6.2 Hz); 7.93–8.20 (m, 4 H, 3 CH_{pyr} and C(2)H); 8.76 (dd, 1 H, CH_{Ar},** *J* **= 8.7 Hz,** *J* **= 2.2 Hz); 8.99 (d, 2 H, 2 CH_{Ar},** *J* **= 2.2 Hz). ¹³C NMR, \delta: 104.75, 113.69, 117.51, 118.33, 119.60, 122.23, 130.04, 131.73, 138.80, 139.56, 140.00, 143.87, 147.71, 151.85. MS, found:** *m/z* **336.0723 [M + H]⁺. C₁₆H₉N₅O₄. Calculated: [M + H] = 336.0727.**

Ethyl 2-cyano-4-(1-[2,4-dinitrophenyl]pyridin-4(1*H*)-ylidene)but-2-enoate (9h). Yield 146 mg (38%), dark violet crystals, m.p. 219–221 °C. IR, v/cm⁻¹: 2202 (CN), 1689 (C=O). UV (CH₂Cl₂), λ_{max} /nm (lgɛ): 468 (4.27), 499 (4.24). ¹H NMR, δ: 1.23 (t, 3 H, CO₂CH₂CH₃, *J* = 7.0 Hz); 4.14 (q, 2 H, CO₂CH₂CH₃, *J* = 7.0 Hz); 5.84 (d, 1 H, C(3)H, *J* = 13.8 Hz); 6.90 (d, 1 H, CH_{pyr}, *J* = 7.1 Hz); 7.35 (d, 1 H, CH_{pyr}, *J* = 7.1 Hz); 7.70–7.86 (m, 2 H, 2 CH_{pyr}); 8.08–8.26 (m, 2 H, CH_{Ar} and C(2)H); 8.74 (dd, 1 H, CH_{Ar}, *J* = 8.8 Hz, *J* = 2.4 Hz); 8.98 (d, 1 H, CH_{Ar}, *J* = 2.4 Hz). ¹³C NMR, δ: 14.90, 60.28, 104.43, 112.90, 118.15, 122.29, 129.96, 131.43, 137.87, 138.49, 140.15, 143.83, 147.40, 148.74, 151.03, 165.42. MS, found: *m*/z 383.0979 [M + H]⁺. C₁₈H₁₄N₄O₆. Calculated: [M + H] = 383.0986.

References

- V. Z. Shirinian, A. A. Shimkin, in *Topics in Heterocyclic Chemistry*, Springer, Berlin-Heidelberg, 2008, pp. 75–105.
- 2. A. V. Kulinich, A. A. Ishchenko, *Russ. Chem. Rev.*, 2009, **78**, 141.
- V. Z. Shirinian, I. V. Zavarzin, E. S. Leonova, A. I. Markosyan, *Mendeleev Commun.*, 2015, 25, 262.
- A. V. Kulinich, N. A. Derevyanko, A. A. Ishchenko, *Russ. J. Gen. Chem.*, 2006, **76**, 1441.
- I. V. Kurdyukova, A. A. Ishchenko, N. A. Derevyanko, D. D. Mysyk, *Chem. Heterocycl. Compd.*, 2013, 49, 281.
- N. A. Davidenko, Yu. P. Get'manchuk, E. V. Mokrinskaya, L. N. Gumenyuk, V. A. Pavlov, N. G. Chuprina, N. N. Kuranda, S. V. Khutornyi, A. A. Ishchenko, N. A. Derevenko, A. V. Kulinich, V. V. Kurdyukov, L. I. Kostenko, *J. Opt. Technol.*, 2008, **75**, 182.

- A. V. Kulinich, N. A. Derevyanko, A. A. Ishchenko, J. Photochem. Photobiol., A, 2007, 188, 207.
- 8. S. Ikeda, H. Yanagisawa, A. Nakamura, D. O. Wang, M. Yukia, A. Okamoto, *Org. Biomol. Chem.*, 2011, **9**, 4199.
- A. A. Vasilev, S. Baluschev, D. Cheshmedzhieva, S. Ilieva, O. D. Castano, J. J. Vaquero, S. E. Angelova, K. Landfester, *Aust. J. Chem.*, 2015, 68, 1399.
- M. V. Fomina, A. S. Nikiforov, S. P. Gromov, *Russ. Chem. Rev.*, 2016, **85**, 684.
- O. G. Nikolaeva, A. V. Metelitsa, A. S. Cheprasov, O. Yu. Karlutova, A. G. Starikov, A. D. Dubonosov, V. A. Bren', V. I. Minkin, *Russ. Chem. Bull.*, 2016, 65, 944.
- 12. I. A. Borisova, A. A. Zubarev, L. A. Rodinovskaya, A. M. Shestopalov, *Arkivoc*, 2017, Part iii, 73.
- I. A. Borisova, A. A. Zubarev, L. A. Rodinovskaya, A. M. Shestopalov, *Russ. Chem. Bull.*, 2018, 67, 168.
- M. Strell, W. B. Braunburck, L. Reithmayr, Justus Liebigs Ann. Chem., 1954, 587, 195.
- A. Kakehi, S. Ito, K. Matsubara, Bull. Chem. Soc. Jpn., 1995, 68, 2409.
- A. Kakehi, S. Ito, T. Funahashi, N. Ogasawara, *Chem. Lett.*, 1975, 4, 919.
- Y. Tominaga, H. Fujito, K. Mizuyama, Y. Matsuda, G. Kobayashi, *Chem. Pharm. Bull.*, 1977, 25, 1519.

- A. Kakehi, I. Suketaka, T. Ohizumi, T. Maeda, J. Org. Chem., 1982, 47, 369.
- W. H. Hao, P. Yan, G. Li, Z. Y. Wang, *Dyes Pigm.*, 2014, 111, 145.
- 20. A. J. Kay, A. D. Woolhouse, G. J. Gainsford, T. G. Haskell, T. H. Barnes, I. T. McKinnie, C. P. Wyss, *J. Mater. Chem.*, 2001, **11**, 996.
- C. J. MacNevin, D. Gremyachinskiy, C.-W. Hsu, L. Li, M. Rougie, T. T. Davis, K. M. Hahn, *Bioconjugate Chem.*, 2013, 24, 215.
- 22. B. P. Bespalov, A. G. Abolin, V. G. Rumyantsev, Chem. Heterocycl. Compd., 1985, 21, 501.
- B. J. Coe, J. A. Harris, I. Asselberghs, A. Persoons, J. C. Jeffery, L. H. Rees, T. Gelbrich, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1999, **20**, 3617.
- 24. L. Ding, H. Li, Y. Zhang, K. Zhang, H. Yuan, Q. Wu, Y. Zhao, Q. Jiao, D. Shi, *RSC Adv.*, 2015, 5, 21415.
- 25. M. D. Khidre, El-S. M. A. Yakout, M. R. H. Mahran, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **133**, 119.

Received June 8, 2018; in revised form July 31, 2018; accepted August 16, 2018