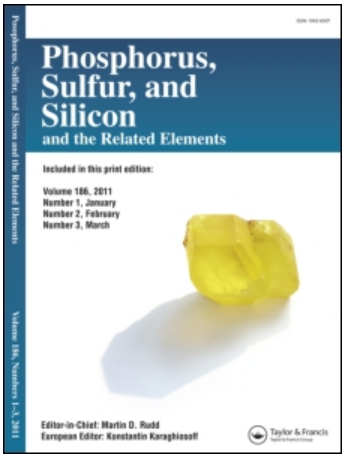

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Spiro-Azoles Thiazolidinone in the Synthesis of Polymethine Cyanine Dyes

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SPIRO-AZOLES THIAZOLIDINONE IN THE SYNTHESIS OF POLYMETHINE CYANINE DYES

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A series of some spiro azoles (pyrazolone, oxazolone, and/or imidazolone) inconjucton with heterocyclic thiazolidinone derivatives were prepared as starting materials in the synthesis of polymethine cyanine dyes. Reaction of spiro 2-formyl (oxime) azoles thiazolidinone derivatives with equi- and/or molar ratios of 2(4)-methyl substituted heterocyclic quaternary salts afforded the corresponding compound pentamethine, aza-mero cyanine, and azapentamethine cyanine dyes respectively. Elemental analyses, IR, ^{1}H-NMR, and mass-spectra identified the new spiro heterocyclic compounds and polymethine cyanine dyes. The visible absorption spectra of all new polymethine cyanine dyes were investigated.

Keywords: Electronic absorption spectra; photodynamic therapy; quaternary salts; sensitizer in photographic

Much work has been carried out on the synthesis of assembled heterocyclic systems to prepare and study the properties of different types of cyanine dyes.[1–5] Little attention has been focused on the use of spiro heterocycles in the synthesis of polymethine cyanine dyes. Thiazolidinone compounds have been subjects of extensive efforts in the recent past of Divers biological activities,[6,7] such as bactericidal, fungicidal, insecticide, tuberoculostic, that are associated with thiazolidinone derivatives. Cyanine dyes are used as spectral sensitizer in photographic emulsions[8] and as potentail sensitizer for photodynamic therapy.[9] In recent years, some patents have reported that pentamethine cyanine dyes showing good sensitivity and reflection to ~680 nm wavelength laser.[10–12]

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TABLE I Characterization Data of Heterocyclic Compounds **2a–2e**, **3a–3e**, and **4a–4e**

Compd. no.	Mol. formula (mol. wt)	Calcd %, Found %			Yield (%)	m.p. (°C)	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H-NMR ($CDCl_3$)	
		C	H	N				δ Assignment	M^+
2a	$C_{16}H_{13}N_3O_2$	68.82	4.66	15.05	95	146–8	3340 (OH)	1.08 (s, 3H, CH_3 pyrazol.)	280
	(279)	68.51	4.77	14.79			1580 (=CN)	4.5 (s, 1H, OH)	
							1690 (C=O)	6.9–7.8 (m, 9H, Ar.—H)	
2b	$C_{20}H_{15}N_3O_2$	72.75	4.56	12.77	93	237–9			
	(329)	72.65	4.71	12.57					
2c	$C_{20}H_{15}N_3O_2$	72.75	4.56	12.77	68	286–8	3340 (OH)	1.09 (s, 3H, CH_3 pyrazol.)	328
	(329)	72.47	4.41	12.63			1585 (C=N)	4.6 (s, 1H, OH)	
							1698 (C=O)	6.8–7.8 (m, 11H, Ar.—H)	
2d	$C_{14}H_{10}N_2O_3$	66.14	3.94	11.02	87	130–2	3340 (OH)	1.2 (s, 1H, CH_3 oxazol)	253
	(254)	66.01	4.15	11.33			1585 (C=N)	4.7 (s, 1H, OH)	
							1698 (C=O)	6.85–7.8 (m, 6H, Ar.—H)	
2e	$C_{14}H_9N_3O_3$	62.92	3.37	15.73	73	110–2		8.7 (s, 2H, 2NH), 4.8 (s, 1H, OH)	
	(267)	63.19	3.11	15.43				6.9–7.75 (m, 6H, Ar.—H)	
3a	$C_{18}H_{15}N_3O_3S$	61.19	4.25	11.90	76	117–9	3350 (OH)	1.1 (s, 3H, CH_3 pyrazol.)	
	(353)	60.89	4.01	12.21			1595 (C=N)	4.5 (s, 1H, OH)	
							1690 (C=O)	6.7–7.8 (m, 11H, Ar.—H + het.—H)	
3b	$C_{22}H_{17}N_3O_3S$	65.51	4.22	10.42	77	132–4	3350 (OH)	1.1 (s, 3H, CH_3 pyrazol.)	
	(403)	65.87	3.99	10.23			1595 (C=N)	4.5 (s, 1H, OH)	
							1690 (C=O)	6.7–7.8 (m, 13H, Ar.—H + het.—H)	
3c	$C_{22}H_{17}N_3O_3S$	65.51	4.22	10.42	75	212–4			
	(403)	65.17	4.49	10.03					

3d	$C_{16}H_{12}N_2O_4S$	58.54	3.66	8.54	74	112–4		1.2 (s, 1H, CH_3 oxazol)
	(328)	59.01	3.75	8.63				4.7 (s, 1H, OH)
								6.7–7.8 (m, 8H, Ar.–H)
3e	$C_{16}H_{11}N_3O_4S$	56.31	3.23	12.32	79	86–8		
	(341)	56.69	3.35	12.55				
4a	$C_{19}H_{14}N_3O_3SCl$	57.07	3.50	10.51	67	181–3	1735 (CHO)	1.1 (s, 3H, CH_3 pyrazol.)
	(399.5)	56.89	3.53	10.67			1690 (C=O)	4.7 (s, 1H, OH), 9.5 (s, 1H, CHO)
							1230 (C–N–C)	6.7–7.8 (m, 9H, Ar.–H + het.–H)
4b	$C_{23}H_{16}N_3O_3SCl$	62.32	3.56	9.34	81	210–2		
	(449.5)	62.43	3.71	9.19				
4c	$C_{23}H_{16}N_3O_3SCl$	62.32	3.56	9.34	79	254–6		
	(449.5)	62.63	3.31	9.69				
4d	$C_{17}H_{11}N_2O_4SCl$	54.47	2.94	7.48	55	175–7	1735 (CHO)	1.2 (s, 1H, CH_3 oxazol)
	(374.5)	54.69	3.11	7.39			1690 (C=O)	4.7 (s, 1H, OH), 9.7 (s, 1H, CHO)
							1230 (C–N–C)	6.7–7.8 (m, 6H, Ar.–H)
4e	$C_{17}H_{10}N_3O_4SCl$	52.65	2.58	10.84	49	1180–2	1730 (CHO)	8.7 (s, 2H, 2NH), 4.8 (s, 1H, OH)
	(387.5)	52.49	3.01	10.55			1698 (C=O)	6.9–7.75 (m, 6H, Ar.–H), 9.7 (s, 1H, CHO)
							1235 (C–N–C)	

The object of this investigation is to report the synthesis and electronic absorption spectra in ethanolic solution in the hope that we might discover new photosensitization effects.

Results and Discussion

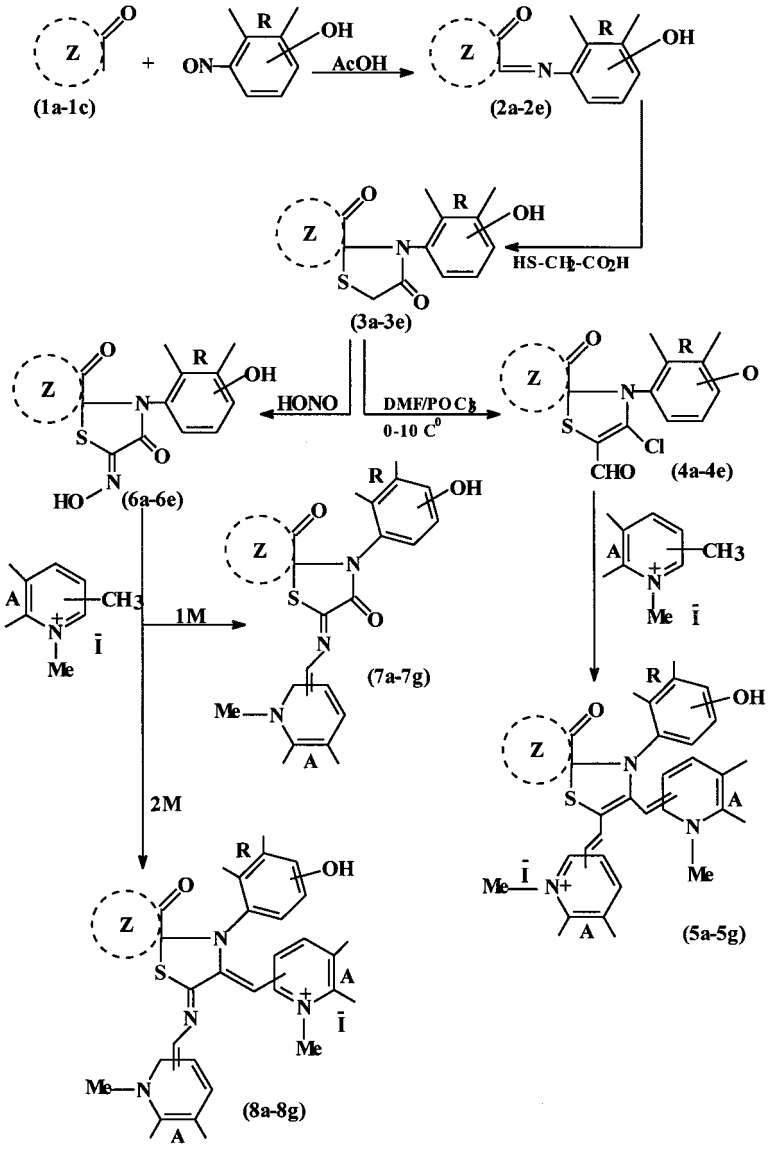
Reaction of 1 mmol amount ratio of 3-methyl-1-phenylpyrazol-5-one, 2-methyoxazol-5-one and imidazol-2,4-dione **1a–1c**[13] with 1 mmol amounts of nitroso compounds such as p-nitrosophenol and a (β)-nitroso-naphthols in basic catalyst afforded the corresponding of 4-aryl (naphthyl)-imino-azole derivatives **2a–2e** as Shiff base compounds. Elemental analyses, IR, ^{1}H-NMR, and MS spectral were confirmed the structures of compounds **2a–2e**. Thus, IR showed general absorption spectra at 1698–1690 cm^{-1} (C=O), 1585 cm^{-1} (C=N), 3340–3360 cm^{-1} (OH), ^{1}H-NMR ($CDCl_3$) reveal general signals at δ 4.5–4.7 (s, 1H, OH), 1.0–1.1 (s, 3H, CH_3), 6.9–7.8 (m, 9H, Ar—H) for compound **2a** and 6.7–7.7 (m, 11H, Ar—H) for compound **2b**, Table I. The newly synthesized Shiff base compounds **2a–2e** were considered as structures for the synthesis of new spiro-4-azolo thiazolidinone derivatives. Thus, cycloaddition reaction of equimolar ratio of thioglycolic acid with the previously compounds **2a–2e** in boiling benzene using water separator for five days[14] afforded the spiro-4-azolo thiazolidinone derivatives **3a–3e**. The structures of these compounds were proved by elemental analyses, IR, ^{1}H-NMR, and MS spectral data. Thus, IR showed general absorption spectra at 1698–1690 cm^{-1} (C=O), 1585 cm^{-1} (C=N), 3340–3360 cm^{-1} (OH), ^{1}H-NMR ($CDCl_3$) reveal general signals at 4.6–4.9 (s, 1H, OH), 6.8–7.9 (m, 8H, Ar—H + het.—H), 1.25 (s, 3H, CH_3), for compound **3d** and 8.7 (s, 2H, NH), for compound **3e**, Table I. Compounds **3a–3e** treated with phosphorus oxychloride in dimethylformamide in the room temperature afforded the corresponding compounds 4-chloro-5-formyl spiro-4-azolo thiazolidinone derivatives **4a–4e**. Reaction of a ratio of 1 mmol amount **4a–4e** with 2 mmol amounts of 2(4)-methyl substituted heterocyclic quaternary salts in the presence of acetic anhydride[16] resulted in pentamethine cyanine dyes **5a–5g**. The structures of compounds **4a–4e** and **5a–5g** were confirmed by elemental analyses, IR, ^{1}H-NMR, and MS spectral data, Tables I and II.

Reaction of spiro-4-azolo thiazolidinone derivatives **3a–3e** with nitrous acid afforded the corresponding compounds 2-oxime-spiro-4-azolo thiazolidinone derivatives **6a–6e**. These newly synthesized oxime compounds **6a–6e** were considered as a key intermediate in the synthesis of aza-mero cyanine dyes **7a–7g** and aza-pentamethine cyanine dyes **8a–8g** respectively. Thus, reaction of a ratio of 1 mmol amount of 2-oxime-spiro-4-azolo thiazolidinone derivatives **6a–6e** with 1 or 2 mmol

TABLE II Characterization Data of Intermediate Compounds **5a–5f** and Heptamethine Cyanine Dyes **6a–6f**

Compd. no.	Mol. formula (mol. wt)	Calcd %, Found % C	H	N	Yield (%)	m.p. (°C)	IR (ν_{max}^{KBr}) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ Assignment	M^+
5a	$C_{33}H_{30}N_5O_2SI$ (687)	57.64 57.07	4.37 4.45	10.19 10.34	57	120–2	860–840 (CH═CH) 1698 (C═O) 2940 (CH_3I)	6.5–7.8 (m, 20H, Ar—H + CH═CH), 4.5 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+) 1.25 (s, 3H, CH_3), 1.09 (s, 3H, CH_3)	
5b	$C_{41}H_{34}N_5O_2SI$ (787)	62.52 62.11	4.32 4.51	8.90 9.03	89	173–5	860–840 (CH═CH) 1690 (C═O) 2960 (CH_3I)		
5c	$C_{33}H_{30}N_5O_2SI$ (687)	57.64 57.17	4.37 4.25	10.19 10.43	67	135–7			
5d	$C_{45}H_{36}N_5O_2SI$ (837)	64.52 64.37	4.30 4.59	8.36 8.21	85	142–4	860–840 (CH═CH) 1690 (C═O) 2960 (CH_3I)	6.6–7.8 (m, 26H, Ar—H + CH═CH), 4.6 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+) 1.4 (s, 3H, CH_3), 1.1 (s, 3H, CH_3)	
5e	$C_{45}H_{36}N_5O_2SI$ (837)	64.52 64.67	4.30 4.55	8.36 8.31	87	210–2			
5f	$C_{39}H_{31}N_4O_3SI$ (762)	61.42 61.67	4.07 4.43	7.35 7.13	73	177–9	860–840 (CH═CH) 1690 (C═O) 2960 (CH_3I)	6.5–7.7 (m, 21H, Ar—H + CH═CH), 4.6 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+) 1.4 (s, 3H, CH_3), 1.2 (s, 3H, CH_3)	
5g	$C_{39}H_{30}N_5O_3SI$ (775)	60.39 60.75	3.87 4.01	9.03 8.91	79	172–4	860–840 (CH═CH) 1690 (C═O) 2960 (CH_3I)	6.6–7.8 (m, 21H, Ar—H + CH═CH), 8.5 (s, 2H, 2NH), 4.7 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+), 1.25 (s, 3H, CH_3)	
6a	$C_{18}H_{14}N_4O_4S$ (382)	56.55 56.77	3.67 3.33	14.66 14.25	77	124–6	1640 (C═N-oxime) 1690 (C═O) 3650–3500 (OH)	6.9–7.8 (m, 9H, Ar—H), 4.8 (s, 1H, OH), 9.8 (s, 1H, C═N—OH), 1.05 (s, 3H, CH_3)	383
6b	$C_{22}H_{16}N_4O_4S$ (432)	61.11 60.97	3.70 4.03	12.96 12.85	81	146–8			
6c	$C_{22}H_{16}N_4O_4S$ (432)	61.11 61.37	3.70 4.13	12.96 12.75	71	230–2			
6d	$C_{16}H_{11}N_3O_5S$ (357)	53.78 53.39	3.08 2.89	11.77 12.09	69	77–9	1630 (C═N-oxime) 1700 (C═O) 3650–3500 (OH)	7.1–7.9 (m, 6H, Ar—H), 4.6 (s, 1H, OH), 10.5 (s, 1H, C═N—OH), 1.2 (s, 3H, CH_3)	356
6e	$C_{16}H_{10}N_4O_5S$ (370)	51.89 51.93	2.70 3.05	15.14 14.93	68	128	1640 (C═N-oxime) 1690 (C═O) 3650–3500(OH)	7.0–7.8 (m, 6H, Ar—H), 4.7 (s, 1H, OH), 9.7 (s, 1H, C═N—OH), 8.5 (s, 2H, 2NH)	

amounts of 2(4)-methyl heterocyclic quaternary salts in the presence of basic catalyst afforded the corresponding spiro-4-azolo thiazolidinone-4[2(4)] aza-mero cyanine dyes **7a–7g** and 4,5[2(4)]-aza-pentamethine cyanine dyes **8a–8g** respectively (Scheme 1). Elemental analyses and



SCHEME 1

IR and ^{1}H-NMR spectra confirmed the structures of compounds **7a–7g** and **8a–8g**. Thus, IR showed general absorption spectra of compounds **7a–7g** and **8a–8g** 1700–1690 cm^{-1} (C=O), 1590 cm^{-1} (C=N), 3340 cm^{-1} (OH), 2980 cm^{-1} (Mel) and ^{1}H-NMR ($CDCl_3$) reveal general signals at 4.6 (s, 1H, OH), 6.5–7.8 (m, 13H, Ar—H + CH=), 1.25 (s, 3H, CH_3), 1.15 (s, 3H, CH_3) for compound **7f** and 4.7 (s, 1H, OH), 6.6–7.9 (m, 20H, Ar—H + CH=), 1.2 (s, 3H, CH_3), 1.15 (s, 3H, CH_3) 3.9 (s, 3H, CH_3 N^+) for compound **8f** (Table III).

The newly synthesized pentamethine **5a–5g**, aza-merocyanine dyes **7a–7g** and aza-pentamethine cyanine dyes **8a–8g** were highly colored and fairly soluble in polar organic solvents giving a green fluorescence. These cyanine dyes were only sparingly soluble in nonpolar solvents and soluble in conc. H_2SO_4 liberating iodine vapor on warming.

Effect of Molecular Structure on the Electronic Absorption Spectra of the Synthesized Cyanine Dyes

The electronic absorption spectral features ($_{max.}$ and $_{max.}$ values) of the newly synthesized cyanine dyes **5a–5g**, **7a–7g**, and **8a–8g** in ethanolic solutions are depicted in Table IV.

The visible absorption spectra of pentamethine cyanine dyes **5a–5g**, aza-mero cyanine **7a–7g**, and aza-pentamethine cyanine dyes **8a–8g** in 95% ethanol undergo bathochromic or hypsochromic shifts depending on the nature of the quaternary residue A. Thus, substituting of A = 1-methylpyridin-2-ium salt moiety in compound **5a** by A = 1-methylquinolin-2-ium salt moiety in compound **5b** resulted in bathochromic shifts of 15–195 nm accompanied with the appearance of one band at 585 nm. This could be attributed to the more extensive -conjugation in compound **5b**. Also, the visible absorption spectra of the newly synthesized cyanine dyes were influenced by the aryl and naphthyl groups. Thus, substituting of R = aryl moiety in compound **7b** by the R = naphthyl moiety in compound **7d** causes bathochromic shifts of 5–45 nm. This is due to increasing the conjugation in compound **7d** (Table IV).

EXPERIMENTAL

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Center at Cairo University. Infrared were determined on a Perkin Elmer Infrared 1650 FT-IR instrument, visible spectra (300–700 nm) were recorded on a Shimadzu-UV-Visible-160 spectrophotometer. ^{1}H-NMR spectra were recorded on an EM-390 90 MHz

TABLE III Characterization Data of Aza-Mero **7a–7g** and Aza-Pentamethine Cyanine Dyes **8a–8gf**

Compd. no.	Mol. formula (mol. wt)	Calcd %, Found % C	H	N	Yield (%)	m.p. (°C)	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H-NMR($CDCl_3$) δ Assignment
7a	$C_{25}H_{21}N_5O_3S$ (471)	63.69 63.47	4.46 4.37	14.86 14.64	78	210–2	1590 (C=N) 1700 (C=O) 3340 (OH)	6.7–7.8 (m, 14H, Ar–H + CH=N), 4.5 (s, 1H, OH), 1.25 (s, 3H, CH_3), 1.09 (s, 3H, CH_3)
7b	$C_{29}H_{23}N_5O_3S$ (521)	66.80 66.71	4.42 4.53	13.44 13.13	83	144–6		
7c	$C_{25}H_{21}N_5O_3S$ (471)	63.69 63.79	4.46 4.27	14.86 15.04	75	230–2		
7d	$C_{33}H_{25}N_5O_3S$ (571)	69.35 68.97	4.38 4.55	12.26 11.95	77	160–2	1590 (C–N) 1700 (C=O) 3340 (OH)	6.6–7.8 (m, 18H, Ar–H + CH=N), 4.6 (s, 1H, OH), 1.3 (s, 3H, CH_3), 1.1 (s, 3H, CH_3)
7e	$C_{33}H_{25}N_5O_3S$ (571)	69.35 69.67	4.38 4.25	12.26 12.35	79	190–2		
7f	$C_{27}H_{20}N_4O_4S$ (496)	65.32 65.27	4.03 3.88	11.29 11.11	75	120–2	1590 (C=N) 1698 (C=O) 3360 (OH)	6.5–7.8 (m, 13H, Ar–H + CH=N), 4.6 (s, 1H, OH), 1.4 (s, 3H, CH_3), 1.2 (s, 3H, CH_3)
7g	$C_{27}H_{19}N_5O_4S$ (509)	63.65 63.55	3.73 4.09	13.75 13.93	82	142–4	1585 (C=N) 1690 (C=O) 3400 (OH, NH)	6.4–7.8 (m, 13H, Ar–H + CH=N), 8.5 (s, 2H, 2NH), 4.7 (s, 1H, OH), 1.2 (s, 3H, CH_3)
8a	$C_{32}H_{29}N_6O_2SI$ (688)	55.81 56.17	4.22 4.63	12.21 12.55	85	240–2	1580 (C=N) 1690 (C=O) 2960 (CH_3I)	6.4–7.8 (m, 19H, Ar–H + CH=CH), 4.6 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+) 1.2 (s, 3H, CH_3), 1.07 (s, 3H, CH_3)

8b	$C_{36}H_{31}N_6O_2SI$	58.54	4.20	11.38	87	162–4		
	(738)	58.87	4.53	11.15				
8c	$C_{32}H_{29}N_6O_2SI$	55.81	4.22	12.21	71	230–2		
	(688)	56.19	4.43	12.53				
8d	$C_{44}H_{35}N_6O_2SI$	63.01	4.18	10.02	87	162-4	1585 (C=N)	6.5–7.7 (m, 25H, Ar–H + CH=CH),
	(838)	62.79	4.41	9.85			1697 (C=O)	4.7 (s, 1H, OH), 3.95 (s, 3H, CH_3N^+)
							2940 (CH_3I)	1.3 (s, 3H, CH_3), 1.09 (s, 3H, CH_3)
8e	$C_{44}H_{35}N_6O_2SI$	63.01	4.18	10.02	83	183-5		
	(838)	62.87	4.11	10.23				
8f	$C_{38}H_{30}N_5O_3SI$	59.76	3.93	9.17	81	165-7	1580 (C=N)	6.6–7.8 (m, 20H, Ar–H + CH=CH),
	(763)	60.07	4.13	9.33			1700 (C=O)	4.8 (s, 1H, OH), 3.9 (s, 3H, CH_3N^+)
							2960 (CH_3I)	1.2 (s, 3H, CH_3), 1.1 (s, 3H, CH_3)
8g	$C_{38}H_{29}N_6O_3SI$	58.76	3.74	10.83	93	150-2	1590 (C=N)	6.5–7.8 (m, 20H, Ar–H + CH=CH),
	(776)	58.53	3.93	10.77			1690 (C=O)	8.5 (s, 2H, 2NH), 4.7 (s, 1H, OH),
							2950 (CH_3I)	3.9 (s, 3H, CH_3N^+), 1.2 (s, 3H, CH_3)

TABLE IV Visible Absorption Spectra[a] of the Newly Synthesized Polymethine Cyanie Dyes

λ_{max} (nm)/log ε_{max} mol^{-1} cm^{-1}						
I Pentamethine cyanine dyes **5a–5g**						
5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
400 (3.50)	415 (3.66)	420 (3.65)	—	—	—	—
—	—	—	525 (3.66)	520 (3.32)	—	510 (3.78)
—	—	—	565 (3.72)	—	—	555 (3.89)
—	585 (3.68)	—	600 (3.70)	590 (3.95)	580 (3.91)	585 (3.93)
—	690 (2.98)	—	700 (2.02)	695 (3.22)	695 (2.05)	695 (3.45)
II Aza-mero cyanine dyes **7a–7g**						
7a	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**
465 (3.08)	sh415 (3.53)	485 (2.95)	sh420 (3.37)	sh410 (3.33)	—	sh410 (3.28)
—	485 (3.51)	—	530 (3.45)	520 (3.35)	—	525 (3.16)
—	590 (3.56)	—	595 (3.46)	590 (3.46)	585 (3.11)	565 (3.29)
—	—	—	—	—	605 (3.15)	610 (3.33)
—	680 (2.90)	—	685 (2.85)	680 (2.92)	680 (2.68)	680 (2.65)
III Aza-pentamethine cyanine dyes **8a–8g**						
8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**
—	sh410 (3.64)	—	420 (3.53)	sh400 (3.51)	—	sh410 (3.81)
480 (3.38)	sh520 (3.77)	490 (3.45)	540 (3.57)	540 (3.75)	sh520 (3.79)	575 (4.13)
—	595 (3.88)	—	595 (3.60)	585 (3.85)	590 (3.80)	595 (4.14)
—	695 (3.30)	—	700 (2.88)	690 (2.78)	690 (2.90)	695 (3.32)

[a]Data shown are $_{max}$ $_{max}$ = $\log_{max}$ (mol^{-1} cm^2) in parentheses; sh = shoulder.

NMR spectrometer and mass spectra were recorded on an HPMs 6988 spectrometer.

Synthesis of 4-Aryl(naphthyl)-imino-azole Derivatives 2a–2e

A solution of 3-methyl-1-phenylpyrazolone, 2-methyloxazolone, and imidazolone (0.01 mmol) in ethanol (20 ml) was treated with aromatic nitroso compounds (p-nitroso-phenol and ( )-nitroso-naphthol) (0.01 mmol) in the presence of catalytic amount of piperidine (0.5 ml). The reaction mixture was refluxed for 7–9 h (monitored TLC). The solvent was then evaporated under reduced pressure and the residue was treated with ice-water. The solid product was collected and crystallized from ethanol. The results are listed in Table I.

Synthesis of Spiro-4-azolo Thiazolidinone Derivatives 3a–3e

A mixture of the imino derivatives **2a–2e** and mercaptoacetic acid (0.01 mmol) in dry benzene was refluxed for 13–15 h. The hot reaction mixture was filtered, concentrated, and boiling water was added. The solid product was collected and crystallized from methanol. Relevant data are listed in Table I.

Synthesis of 3-Chloro-2-formyl-spiro-4-azolo Thiazolidinone Derivatives 4a–4e

To a solution of **3a–3e** (0.02 mmol) in (100 ml) dry dimethylformamide and phosphorous oxychloride (0.02 mmol) was added under stirring in an ice-bath. Stirring was continued at room temperature for 15 min. The solution was heated for 30 min, cooled, and then poured into 400 ml ice-water. The solid product was collected and crystallized from petroleum ether 60–80°C. Relevant data are listed in Table I.

Synthesis of Spiro-4-azolo Thiazolidinone-2,3[2(4)]-pentamethine Cyanine Dyes 5a–5g

A mixture of **4a–4e** (0.01 mmol) and 2(4)-methyl heterocyclic quaternary salts (0.02 mmol) were dissolved in acetic anhydride (10 ml). The reaction mixture was refluxed for 5–10 min, and the excess of acetic anhydride was distilled off. The cooled residue was triturated with ethanol, then filtered while hot and concentrated. The precipitated products, after dilution with water, were collected and crystallized from methanol. The characterization data of compounds **5a–5g** are listed in Table II.

Synthesis of 2-Oxime-spiro-4-azolo Thiazolidinone Derivatives 6a–6e

To a solution of **3a–3e** (0.01 mmol) and sodium nitrite (0.02 mmol) in aqueous ethanol (20 ml), conc. sulphuric acid (10 ml) was added drowse while stirring in ice-bath. The stirring was continued at room temperature for 10 min.

The precipitated products after dilution with water were collected and crystallized from ethanol. Relevant data are shown in Table II.

Synthesis of Spiro-4-azolo Thiazolidinone-2[2(4)]-aza-mero Cyanine 7a–7g and 2,3[2(4)]-Aza-pentamethine Cyanine Dyes 8a–8g

A mixture of **6a–6e** (0.01 mmol) and 2(4)-methyl heterocyclic quaternary salts (0.01 and 0.02 mmol) were dissolved in ethanol (20 ml) and piperidine (0.5 ml) was added. The reaction mixture was refluxed for

10–12 h, filtered while hot, concentrated, and cooled. The solid products were separated after dilution with water were collected and crystallized from methanol to give the corresponding compounds **7a–7g** and **8a–8g** respectively. The characterization data of these dyes are listed in Table III.

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