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SYNTHESIS OF 2,2'-QUINOCYANINES WITH LONG N-ALKYL SUBSTITUENTS

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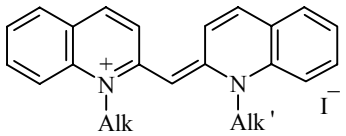
2,2'-Quinocyanines with long alkyl substituents on one or both nitrogen atoms have been synthesized. ^{1}H NMR spectroscopy has been used to study the processes occurring during the alkylation of the starting quinoline bases.

Keywords: N-alkyl groups, 2,2'-quinocyanines, ^{1}H NMR spectroscopy.

Organized molecular groups of organic compounds find use in contemporary systems of recording and processing information [1]. There is great interest in ordered aggregates of cyanine dyes characterized by a highly efficient transfer of excitation energy to heterogeneous molecular systems [2]. Non-linear optical properties have been found in the last decade for *J*-aggregates of polycyanines. Experimentally, the huge value of the non-linear sensitivity for picosecond relaxation times [3] obtained for *J*-aggregates of 1,1'-diethyl-2,2'-quinocyanine* has promoted their consideration as promising media for non-linear optical transformation of light radiation. From a practical viewpoint, the greatest interest is in the known method of obtaining *J*-aggregates of PIC as thin films created without the use of the Langmuir–Blodgett technique [4].

Evidently, the film forming ability and the properties of *J*-aggregate structures depend to a significant degree on the structure of the monomer form of the dye. In our opinion, a positive effect can be achieved by the introduction of a long aliphatic substituent into the dye molecule. In order to check this proposal we have undertaken in this work the synthesis of PIC derivatives of type **1** which contain C_nH_{2n+1} substituents (where $n \geq 10$) at one or at both nitrogen atoms.



1a–f

a Alk = Alk' = $C_{10}H_{21}$, **b** Alk = Alk' = $C_{15}H_{31}$, **c** Alk = Alk' = $C_{18}H_{37}$, **d** Alk = $C_{10}H_{21}$, **e** Alk = $C_{15}H_{31}$, **f** Alk = $C_{18}H_{37}$, **d–f** Alk' = Et

* The trivial name pseudoisocyanine (PIC) is often used in the literature.

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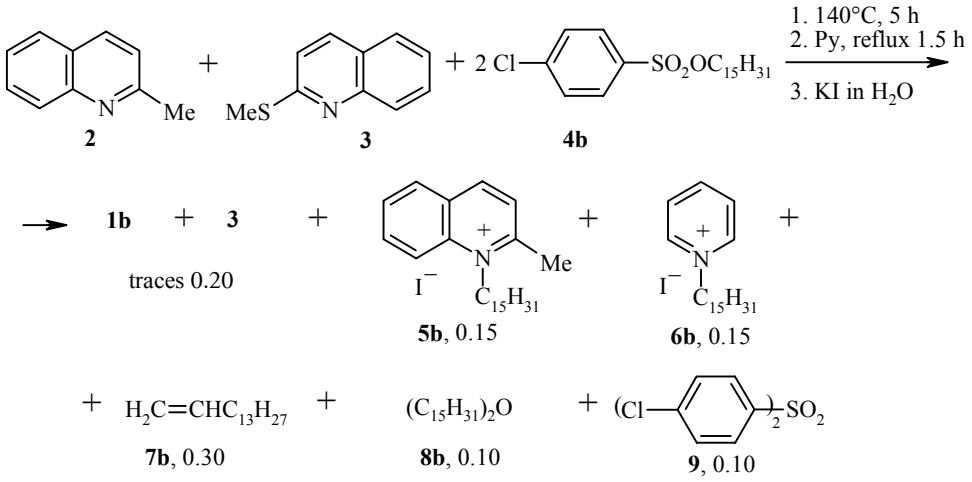
The dye **1c** has been previously described [5] and the synthesis starting from quinaldine (**2**), 2-methylthioquinoline (**3**), and octadecyl *p*-chlorobenzenesulfonate occurred in low yield (~4%). The reaction scheme includes alkylation of the bases **2** and **3** by sulfonate and subsequent condensation in pyridine to give the quaternary salts.

We have repeated this method as applied to the sulfo esters **4a-c** with the general formula *p*-$ClC_6H_4SO_3Alk$ (**a** Alk = $C_{10}H_{21}$, **b** Alk = $C_{15}H_{31}$, **c** Alk = $C_{18}H_{37}$). In all of the examples, multicomponent mixtures were obtained and the yields of the target dyes did not exceed 2-4%. In order to explain the nature and the reason for formation of the side products we have carried out a full analysis of the reaction mixture using ^{1}H NMR spectroscopy.

In most cases the components of the mixture were identified by comparison with samples of the individual compounds separated from the reaction products or those synthesized by an independent route. The results obtained are discussed in detail for the synthesis of dye **1b**. In Scheme 1 the molar composition of the reaction mixtures are given as calculated from the ^{1}H NMR spectrum.

Scheme 1



The simultaneous presence in the mixture of the N-alkylquinaldinium salt **5b** and the starting methylthioquinoline **3** points to the relative difficulty of alkylating the latter. It seems likely that the quaternary salt **6b** is formed in the second stage of the reaction by the alkylation of pyridine. The alkene **7b** and dialkyl ether **8b** are not, in this case, simply the products of thermolysis of the sulfo ester **4b** (cf. [6]) since the latter is stable to heating up to 150°C. It can be proposed that the reaction forming them occurs with participation of a pentadecyl cation (cf. [7]) and this indicates the reversibility of the alkylation reaction. It should be said that, in the example of each of the esters **4a-c,** the alkenes of type **7** were not separated in the pure state and the proposed structures are based on ^{1}H NMR spectrosopic data. These show three typically split signals at 4.9, 5.0, and 5.8 ppm [8]. The presence of the di(*p*-chlorophenyl) sulfone (**9**) in the mixture agrees with known data for the possibility of fission of the alkyl arylsulfonate molecule at the C_{Ar}–S and S–OAlk bonds [9].

The results obtained lead to the proposal that the yield of the target dye can be increased *via* optimization at each stage of carrying out the process. In this connection we have studied the alkylation reactions of the bases **2** and **3** at different temperatures. The analysis of the reaction products was carried out using ^{1}H NMR spectroscopy.

The results for the alkylation of quinaldine **2** by the sulfo esters **4a-c** are given in Table 1 for a wide range of temperatures. It can be seen that the formation of the N-alkyl-substituted quinaldinium salt of type **5** requires heating above 100°C and is at a maximum at 140°C. In all cases the reaction mass is predominantly an

TABLE 1. Composition of the Reaction Mixtures Obtained from the Alkylation of Quinaldine **2** by Sulfo esters **4a-c**, According to ^{1}H NMR Data

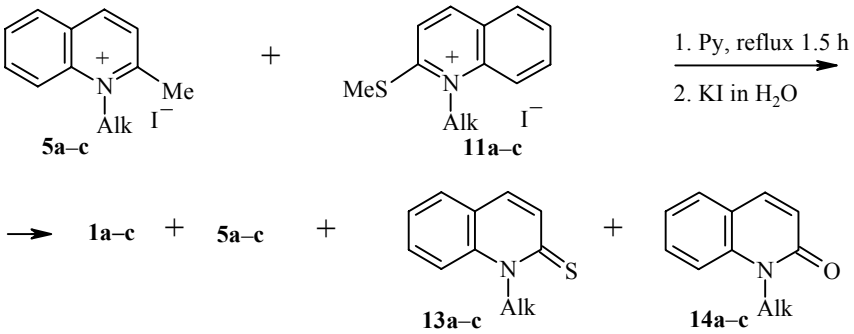
Reaction temp., °C	Content in the reaction mixture, mol %														
	2 + **10**			**4**			**5**			**7**			**8**		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
100	60	50	50	25	45	45	10	5	5	—	—	—	5	—	—
120	45	40	65	10	25	10	25	30	20	—	—	–	20	5	5
140	40	40	40	—	5	—	30	40	30	5	10	20	25	5	10
170	40	40	40	—	—	—	20	35	30	10	20	25	30	5	5
200	55	40	45	—	—	—	15	20	20	10	35	30	20	5	5

equilibrium mixture of quinaldine **2** and quinaldinium *p*-chlorobenzenesulfonate (**10**) as is shown by comparison of the ^{1}H NMR spectra of this mixture with the spectra of compounds **2** and **10** and also their model mixtures. Washing the reaction mixture with ether leaves a mixture of *p*-chlorobenzenesulfonate **10** and the corresponding N-alkylquinaldinium type salt **5**. A small amount of methylene chloride washes out the salt **5** and dilution with aqueous ammonia the salt **10** which is also readily converted to the base **2**.

The protonation of starting compound **2** reported above lowers the yield of the quaternary salt of type **5**. One of the sources of the proton could be a carbonium ion which is formed upon dealkylation of salt **5** and then converts to an alkene of type **7**.

The alkylation of 2-methylthioquinoline **3** is evidently hindered by comparison with the quinaldine **2** as a result of steric hindrance on the side of the bulkier MeS group. The optimum yield of the quaternary salt of type **11** (see Scheme 2) is observed at 170°C and is not more than 11%. In the reaction products obtained under these conditions, an equilibrium mixture of the starting base **3** and its *p*-chlorobenzenesulfonate **12** predominates. The reaction is complicated to a major degree by side processes; in addition to compounds **7** and **8** there are a series of unidentified impurities contained in the products.

Scheme 2



Hence this investigation has shown that one of the basic factors which lowers the yield of the target dye in the conditions of [5] is the reduced reactivity of 2-methylthioquinoline towards alkylation. This results in the need for more forcing conditions when carrying out the reaction and, in turn, to an increase in the proportion of side products.

The target dyes **1a-c** were obtained in low yields (7-20%) by the mutual condensation of the salts **5a-c** and **11a-c** in refluxing pyridine using the known method [5]. ^{1}H NMR Analysis of the reaction mixtures has shown that half of the starting salt **5** is returned unchanged. The presence of significant amounts (0.4-0.5 mole proportion) of the 1-alkylquinoline-2-thione **13a-c** in the products together with traces of the

TABLE 2. Characteristics for the 1-Alkyl-2-methylquinolinium Iodides **5a-c** and 1-Alkyl-2-methylthioquinolinium Iodides **11a-c**

Compound	Alk	Empirical formula	Found, % / Calculated, %					mp, °C	^{1}H NMR spectrum, δ, ppm, SSCC (*J*), Hz								Yield, %
			C	H	I	N	S		CH_3(Alk), t CH_3/CH_3S–Het, s	CH_2(Alk), m	Het						
											3-H, d	4-H, d	5-H, d	6-H, dd	7-H, dd	8-H, d	
5a	$C_{10}H_{21}$	$C_{20}H_{30}IN$	58.02 58.39	7.37 7.35	30.60 30.85	3.49 3.41		120-123	0.82 3.29	1.23 (12H), 1.57 (2H), 1.94 (2H), 5.02*[2]	8.11 (8.0)	9.01 (8.0)	8.29 (7.5)	7.85 (7.5, 7.5)	8.13 (7.5; 9.0)	8.32 (9.0)	22
5b	$C_{15}H_{31}$	$C_{25}H_{40}IN$	62.32 62.41	8.50 8.36	26.30 26.38	3.07 2.91		130-133	0.85 3.31	1.23 (22H), 1.60 (2H), 1.99 (2H), 5.04*[2]	8.14 (8.5)	9.03 (8.5)	8.31 (8.0)	7.87 (8.0; 7.0)	8.16 (7.0; 9.0)	8.33 (9.0)	41
5c*	$C_{18}H_{37}$	$C_{28}H_{46}IN$	64.01 64.23	8.90 8.86	24.50 24.24	2.78 2.67		121-124	0.84 3.24	1.23 (28H), 1.61 (2H), 1.97 (2H), 4.96*[2]	8.11 (8.5)	9.01 (8.5)	8.29 (8.0)	7.84 (8.0; 7.0)	8.13 (7.0; 9.0)	8.31 (9.0)	40
11a	$C_{10}H_{21}$	$C_{20}H_{30}INS$	54.35 54.17	6.60 6.82	28.50 28.62	3.14 3.16	7.30 7.23	113-116	0.87 3.16	1.26 (10H), 1.41 (2H), 1.59 (2H), 1.97 (2H), 4.89*[2]	8.14 (9.0)	9.02 (9.0)	8.22 (7.5)	7.81 (7.5; 7.5)	8.09 (7.5; 9.0)	8.49 (9.0)	4
11b	$C_{15}H_{31}$	$C_{25}H_{40}INS$	58.24 58.46	7.63 7.85	24.90 24.71	2.72 2.73	6.30 6.25	112-115	0.85 3.18	1.23 (20H), 1.40 (2H), 1.60 (2H), 1.96 (2H), 4.88*[2]	8.16 (9.0)	9.02 (9.0)	8.21 (7.5)	7.80 (7.5; 7.5)	8.10 (7.5; 9.0)	8.48 (9.0)	6
11c	$C_{18}H_{37}$	$C_{28}H_{46}INS$	60.62 60.52	7.91 8.34	22.80 22.84	2.58 2.52	5.60 5.77	122-124	0.86 3.18	1.25 (26H), 1.42 (2H) 1.59 (2H), 1.98 (2H), 4.87*[2]	8.09 (9.0)	9.02 (9.0)	8.22 (7.5)	7.81 (7.5; 8.0)	8.09 (8.0; 9.0)	8.53 (9.0)	11

* The *p*-chlorobenzenesulfonate has been reported in [5].

*[2] 2H, br. t.

TABLE 3. Characteristics for the 1-R^1-2-[(1-R^2-2(1H)-Quinolylidene)methyl]quinolinium Iodides **1a-f**

Com-pound*	Emprical fomula	Found, % / Calculated, %				mp, °C	UV spectrum, λ_{max}, nm (log ε)	^{1}H NMR spectrum, δ, ppm										Yield, %, (method)		
								R^1 and R^2		–CH=, s	Het									
		C	H	I	N			CH_3, t	CH_2, m		3- and 3'-H	4- and 4'-H	5- and 5'- H	6- and 6'-H	7- and 7'-H	8- and 8'-H	A	B	C
1a	$C_{39}H_{55}IN_2$	69.36 / 69.01	8.18 / 8.18	18.60 / 18.69	4.37 / 4.13	~130	496 (4.69); 531 (4.90)	0.85 (6H)	1.20-1.35 (20H); 1.40 (4H); 1.58 (4H); 1.90 (4H); 4.41 (4H), br. t	5.48	7.86	8.07	7.71	7.36	7.96	7.63	2	20	30
1b	$C_{49}H_{75}IN_2$	71.95 / 71.86	9.49 / 9.23	15.32 / 15.49	3.58 / 3.42	~150	496 (4.70); 531 (4.92)	0.85 (6H)	1.23-1.40 (40H); 1.45 (4H); 1.60 (4H); 1.96 (4H); 4.42 (4H), br. t	5.50	7.92	8.12	7.77	7.43	7.74	7.63	3	7	50
1c*[2]	$C_{55}H_{87}IN_2$						496 (4.70); 531 (4.91)	0.85 (6H)	1.20-1.40 (52H); 1.44 (4H); 1.60 (4H); 1.95 (4H); 4.41 (4H), br. t	5.46	7.90	8.13	7.78	7.43	7.74	7.63	4	8	70
1d	$C_{31}H_{39}IN$	65.35 / 65.72	6.82 / 6.94	21.93 / 22.40	4.61 / 4.94	~125	495 (4.70); 529 (4.92)	0.84 (3H); 1.63 (3H)	1.20-1.50 (12H); 1.60 (2H); 1.95 (2H); 4.46 (2H) br. t ; 4.58 (2H) br. q	5.55	7.86	8.08	7.76	7.41	7.73	7.63, 7.71	32	22	
1e	$C_{36}H_{49}IN$	67.76 / 67.91	6.82 / 7.76	21.93 / 19.93	2.78 / 4.40	~140	495 (4.68); 529 (4.90)	0.84 (3H); 1.62 (3H)	1.20-1.45 (22H); 1.59 (2H); 1.94 (2H); 4.46 (2H) br. t ; 4.59 (2H) br. q	5.56	7.84	8.07	7.74	7.40	7.73	7.63, 7.71	38	30	
1f	$C_{39}H_{55}IN$	68.75 / 69.01	8.24 / 8.17	18.81 / 18.70	4.27 / 4.13	~145	495 (4.61); 529 (4.83)	0.83 (3H); 1.61 (3H)	1.20-1.40 (28H); 1.60 (2H); 1.94 (2H); 4.44 (2H) br. t ; 4.56 (2H) br. q	5.53	7.85	8.04	7.74	7.40	7.72	7.63, 7.71	43	20	

* **1 a** $R^1 = R^2 = C_{10}H_{21}$, **b** $R^1 = R^2 = C_{15}H_{31}$, **c** $R^1 = R^2 = C_{18}H_{37}$, **d-f** $R^1 = C_2H_5$, **d** $R^2 = C_{10}H_{21}$, **e** $R^2 = C_{15}H_{31}$, **f** $R^2 = C_{18}H_{37}$.

*[2] The perchlorate has been reported in [5].

TABLE 4. Characteristics for the 1-Alkylquinoline-2(1H)-thiones **13a-c, 16** and 1-Alkylquinolin-2(1H)-ones **14a-c, 17**

Compound	Alk	Empirical formula	Found, % / Calculated, %				mp, °C	^{1}H NMR spectrum, δ, ppm, CCSS (*J*), Hz							
								Alk		Het					
			C	H	N	S		CH_3, t	CH_2, m	3-H, d	4-H	5-H, d	6-H, dd	7-H, m	8-H, m
13a	$C_{10}H_{21}$	$C_{19}H_{27}NS$*	—	—	—	—	Oil	0.85	1.20-1.90 (16H), 5.00 (2H), br. t	7.42 (9.0)	7.62, m	7.53 (8.0)	7.32 (8.0; 7.0)	7.63	7.62
13b	$C_{15}H_{31}$	$C_{24}H_{37}NS$	77.64 / 77.57	9.60 / 10.04	3.69 / 3.77	8.70 / 8.63	50-52	0.86	1.20-1.90 (25H), 5.00 (2H), br. t	7.40 (9.0)	7.62, m	7.52 (8.0)	7.30 (8.0; 7.0)	7.60	7.63
13c	$C_{18}H_{37}$	$C_{27}H_{43}NS$	78.31 / 78.39	10.48 / 10.48	3.39 / 3.38	7.80 / 7.80	64-66	0.86	1.20-1.90 (32H), 5.00 (2H), br. t	7.41 (9.0)	7.62, m	7.54 (8.0)	7.32 (8.0; 7.0)	7.64	7.63
16	C_2H_5	$C_{11}H_{11}NS$	69.88 / 69.80	5.89 / 5.86	7.45 / 7.40	16.80 / 16.94	51-53	1.45	5.00 (2H), br. t	7.42 (9.0)	7.62, m	7.57 (8.0)	7.32 (8.0; 7.0)	7.64	7.62
14a	$C_{10}H_{21}$							0.85	1.20-1.60 (14H), 1.71 (2H), 4.25 (2H), br. t	6.67 (9.5)	7.63, d (9.5)	7.33 (8.5)	7.18 (8.5; 7.0)	7.53	7.53
14b	$C_{15}H_{31}$							0.85	1.20-1.45 (24H), 1.72 (2H), 4.26 (2H), br. t	6.68 (9.0)	7.64, d (9.0)	7.34 (8.0)	7.19 (8.0; 7.0)	7.53	7.53
14c	$C_{18}H_{37}$							0.85	1.20-1.45 (30H), 1.72 (2H), 4.25 (2H), br. t	6.67 (9.0)	7.63, d (9.0)	7.33 (8.5)	7.19 (8.5; 7.0)	7.53	7.53
17*[2]	C_2H_5						Oil	1.33	4.34 (2H), q	6.65 (9.5)	7.64, d (9.5)	7.37 (8.5)	7.20 (8.5; 7.0)	7.53	7.53

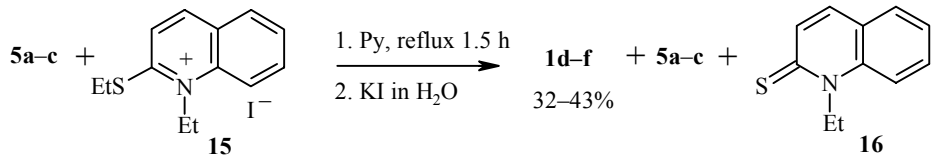
* Found: *m/z* 301.1875 $[M]^+$. Calculated: M = 301.1864.

*[2] Synthesized using the method in [16] and used for the synthesis of compound **1b** without additional purification.

1-alkylquinolin-2-one **14a-c** shows that the reason for the inefficiency of the condensation reaction is the instability of a type **11** salt in these conditions. In fact it was found that they are readily demethylated upon refluxing in pyridine.

We have found that the yield of the dye **1a-c** can be increased to 30-70% by the exchange of pyridine for DMSO with the addition of a small amount of triethylamine.

The unsymmetrical dyes **1d-f** were prepared by the condensation of the salts **5a-c** with 1-ethyl-2-ethylthioquinolinium iodide (**15**) in pyridine. In addition to these, the reaction mixtures contain up to 0.3 mole fraction of the starting salt **5** and 2-ethylquinoline-2-thione (**16**). In these cases an exchange of pyridine for DMSO–Et_3N has no positive effect.



The synthesized dyes **1a-f** were separated in the pure state and their composition was confirmed by elemental analysis, electronic absorption and ^{1}H NMR spectroscopic data. The formation of *J*-aggregate structures based on them and investigation of the non-linear properties of the latter will be presented in a separate publication.

EXPERIMENTAL

IR spectra were recorded on Vector 22 and UR-20 instruments and electronic absorption spectra on a Beckman DU-8 spectrophotometer using methylene chloride (long-wave absorption bands given). ^{1}H NMR spectra were taken on DRX-500 (500 MHz) and WP-200 SY (200 MHz) instruments using $CDCl_3$. The molecular weight was determined mass spectrometrically on a Finnigan MAT model 8200 GC/MS instrument.

Reaction of Quinaldine 2 with the Sulfo Esters 4a-c. A mixture of quinaldine **2** (5.0 mmol) and the sulfoester **4a-c** (5.5 mmol) was held at the temperature indicated in Table 1 for 5 h, cooled, thoroughly mixed, and analyzed by ^{1}H NMR spectroscopy. The results are given in Table 1. After the reaction mixture was washed out with ether the ether solution was chromatographed on an Al_2O_3 column (eluent CH_2Cl_2) collecting the first, light yellow colored fraction. Evaporation then gave the dialkyl ether **8a-c**. The dioctadecyl ether **8c** is identical to that reported in the literature (mp [10] and ^{1}H NMR spectrum [11].

The residue insoluble in ether was a mixture of the *p*-chlorobenzenesulfonates of quinaldine [**10**] and the N-alkyl quinaldine of type **5** and was washed with aqueous ammonia (5%) to remove the salt **10**. The remaining salt was converted to the iodide **5a-c** by reprecipitation from MeCN using aqueous KI solution. The yields and basic parameters for compounds **5a-c** are given in Table 2.

To remove the salt **10** from the mixture indicated above it was washed with a small amount (~5 ml) of CH_2Cl_2, the insoluble residue being reprecipitated from CH_2Cl_2 (~20 ml) using ether. The **Quinaldinium *p*-Chlorobenzenesulfonate (10)** obtained has mp 197-200°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 3.10 (3H, s, CH_3); 7.35 (2H, d, *J* = 8, m-H); 7.63 (1H, d, *J* = 8, 3-H); 7.80 (1H, t, *J* = 8, 6-H); 7.94 (2H, d, *J* = 8, *o*-H); 7.99 (1H, t, *J* = 8, 7-H); 8.02 (1H, d, *J* = 8, 5-H); 8.66 (2H, d, *J* = 8, 4- and 8-H). Found, %: C 57.14; H 4.12; Cl 10.30; N 4.09; S 9.40. $C_{16}H_{14}ClNO_3S$. Calculated, %: C 57.23; H 4.20; Cl 10.56; N 4.17; S 9.55.

Reaction of 2-Methylthioquinoline 3 with the Sulfo Ester (4a-c). A mixture of compound **3** (5.0 mmol) and the sulfoester **4a-c** (5.5 mmol) was held for 5 h at 140, 170, or 200°C, cooled, thoroughly mixed, and analyzed using ^{1}H NMR spectroscopy. The reaction mixture was further washed with ether, then MeCN, and the residue was reprecipitated from CH_2Cl_2 by ether. The **2-Methylthioquinolinium**

***p*-Chlorobenzenesulfonate (12)** obtained has mp 166-169°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.97 (3H, s, SCH_3); 7.35 (2H, d, *J* = 8.0, *m*-H); 7.51 (1H, d, *J* = 9.0, 3-H); 7.68 (1H, t, *J* = 7.5, 6-H), 7.89 (1H, d, *J* = 7.5, 5-H); 7.90-7.94 (3H, m, 7-H, *o*-H); 8.39 (1H, d, *J* = 9.0, 4-H); 8.72 (1H, br. d, *J* = 8.0, 8-H). Found, %: C 52.23; H 4.03; Cl 9.61; N 3.74; S 17.00. $C_{16}H_{14}ClNO_3S_2$. Calculated, %: C 52.24; H 3.84; Cl 9.64; N 3.81; S 17.43.

The solution obtained by washing the mixture with acetonitrile (see above) was poured into aqueous KI solution (20%) and the bright yellow precipitate was filtered off to give the 1-alkyl-5-methylthioquinolinium iodide **11a-c**. This was purified chromatographically on an Al_2O_3 column (eluent CH_2Cl_2–CH_3CN, 4:1) and reprecipitated from CH_2Cl_2 using ether. The yields and basic parameters for the salts **11a-c** are given in Table 2.

Preparation of the Symmetrical Quinocyanines (1a-c). A [5]. A mixture of quinaldine **2** (5 mmol), compound **3** (5 mmol), and the sulfo ester **4** (11 mmol) was held for 5 h at 140°C, cooled to 120°C, dry pyridine added (2 ml), and refluxed for 1.5 h. The reaction mass was cooled, poured into aqueous KI solution (20%), extracted with CH_2Cl_2, the extract washed with hydrochloric acid (2%) and then water and dried over $CaCl_2$. The product was evaporated and the residue analyzed by the ^{1}H NMR spectroscopic method.

Column chromatography of the indicated residue on SiO_2 gave fractions 1-4 in sequence.

Fraction 1 (eluent CH_2Cl_2) was evaporated to give crystals of the sulfone **9** which was identical to a known sample (mp [12] and ^{1}H NMR spectrum) [9].

After repeated chromatography of fraction 2 on SiO_2 (eluent CH_2Cl_2–MeCN, 4:1) the evaporation of the eluate and reprecipitation of the residue from CH_2Cl_2 using ether gave the quinocyanines **1a-c**. The yields and basic parameters for the products **1a-c** are given in Table 3.

Fraction 3 (eluent CH_2Cl_2–MeCN, 1:1) was evaporated to give the quinaldinium iodides **5a-c**.

Fraction 4 (eluent MeCN) was evaporated to give the N-alkylpyridinium iodides **6a-c**. Salt **6c** was identical to that reported in [13] (mp). The ^{1}H NMR spectra for **6a-c** were similar and agreed with the structures for the N-alkylpyridinium salts (cf. [14]).

B. Equimolar amounts of the salts **5a-c** and salts **11a-c** respectively (0.15 mmol of each) were refluxed in dry pyridine (1 ml) for 1.5 h, the reaction mixture was cooled, and worked up as in method A. The residue obtained after evaporation of CH_2Cl_2 was analyzed using ^{1}H NMR.

Chromatography of the indicated residue on a silica column using benzene gave the 1-alkylquinoline-2(1H)-thiones **13a-c**, CH_2Cl_2 gave 1-alkylquinoline-2(1H)-ones **14a-c**, and a mixture of CH_2Cl_2–MeCN (4:1) the quinocyanines **1a-c**. The yields and parameters for compounds **1a-c** are given in Table 3 and the parameters for the thiones **13a-c** and quinolones **14a-c** in Table 4. Compound **13a** is identical in ^{1}H NMR spectrum to a sample synthesized by oxidation of 1-decylquinolinium iodide [15] using potassium ferricyanide in basic medium to the quinolone **14a** (by a known method [16]) and thionylation of the latter with phosphorus pentasulfide using the method in [17].

C. DMSO (1 ml, dried over molecule sieves) and a drop of Et_3N were added to a mixture of equimolar amounts of the salts **5a-c** and salt **11a-c** (0.15 mmol of each) and the obtained product was held at 110-120°C for 1.5 h. It was then cooled, poured into aqueous KI solution (20%), and the precipitate filtered off or extracted with CH_2Cl_2. The separation and purification of product **1** followed that in method A. The yields of compounds **1a-c** are given in table 3.

Preparation of the Unsymmetrical Dyes 1d-f (Table 3). A. (see also the preparation of compounds **1a-c**). A mixture of salt **5a-c** (1 mmol) and compound **15** (1 mmol, synthesized as in method [18]) was refluxed in dry pyridine (1 ml) for 1.5 h and then poured into aqueous KI solution (20%) and worked up as above. Chromatography on an SiO_2 column with CH_2Cl_2 eluent gave 1-ethylquinoline-2(1H)-thione **16** which was identical in mp and ^{1}H NMR spectrum to a sample synthesized by an independent route from 1-ethylquinolinium iodide *via* 1-ethylquinoline-2(1H)-thione (**17**) by the method in [16, 17]. The eluent CH_2Cl_2–MeCN (4:1) gave the quinocyanines **1d-f**.

B. DMSO (1 ml, dried over molecular sieves) and Et_3N (1 drop) were added to a mixture of equimolar amount of salt **5a-c** and salt **15** (1 mmol of each). The reaction mixture was held at 110-120°C for 1.5 h, cooled, and worked up as in method A.

Thermal Reaction of Salt 15 in Pyridine. Compound **15** (0.2 g) was refluxed in pyridine (1 ml) and the reaction mixture was poured into aqueous KI solution (20%), extracted with CH_2Cl_2, and the extract was washed with hydrochloric acid (2%) and water and then dried over $CaCl_2$. After evaporation of solvent the residue was analyzed by the ^1H NMR method. The reaction product was a mixture (10:1) of the thione **14** and quinolinone **17**.

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