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Reference Data

^{1}H and ^{13}C NMR spectra of commercial rhodamine ester derivatives

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ABSTRACT: Ethyl and methyl esters of commercial rhodamines B, 19, 101 and 110 and propyl and butyl esters of commercial rhodamine B were synthesized and isolated with different counterions (yields 70–98%). The ^{1}H and ^{13}C NMR spectral data for these compounds were fully assigned by a combination of one- and two-dimensional experiments. The Fourier transform IR and UV–visible spectra were also recorded and the main bands were identified. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; rhodamine esters

INTRODUCTION

The rhodamines[1] are xanthene derivatives of alkylated *m*-aminophenols. This class of dye shows typically strong fluorescence due to the ring closure by the oxygen atom at the 2,2′-position of the related parent diphenylmethine dyes. Without such a bridge very little or no fluoresce is observed. Therefore, some of the most important applications of this class of dye are based on this high fluorescence yield ($\phi_F \geq 0.7$), the short lifetime of the S_1 state ($\tau F \leq 10$ ns), the little intersystem crossing to triplet states, the strong absorption of the pumping radiation and the high photochemical stability. For instance, rhodamine 6G (the ethyl ester of rhodamine B) was used in one of the first two dye lasers and it is still the dye most frequently used for dye lasers. Rhodamines can also be applied in the textile industry to mordanted cotton and to silk. Recently, other important new applications of rhodamines in the acid or ester form were reported, such as their use as probes and indicators[2] and as dyes for medical and biological applications.[3]

The present work of rhodamine esterifications with low molecular weight alcohols yielded models for cellulose binding, which constitutes an alternative to the use of reactive isothiocyanate rhodamines.[4]

EXPERIMENTAL

Materials

The starting rhodamines were purchased from Aldrich and used as received. The alcohols used were of analytical-reagent grade.

The esterification of rhodamines having carboxylic groups was carried out under Fischer conditions. Typically, the rhodamine was dissolved in a minimum volume of the appropriate alcohol solution containing 3% of sulphuric acid and the resulting solution was then heated with stirring at 50 °C for 1–6 days, until total conversion to the respective ester was achieved. The resulting still highly fluorescent solution was concentrated and the esters were converted into bromide, iodide or perchlorate salts by treatment with an excess of a 14% aqueous solution of potassium iodide, potassium bromide or sodium perchlorate. The ratio between the aqueous and alcoholic solution was kept around 1 : 2. The resulting precipitated dye was filtered off or in some cases the resulting oleum was decanted off, to yield after drying the respective ester in high yield in most cases. No attempts were made to obtain higher yields.

All the reactions were monitored by thin-layer chromatography (TLC) on aluminium sheets precoated with Merck silica gel 60 F_{254} (0.25 mm) using *n*-butanol–water–ethanol (9 : 3 : 1) acidified with 1% acetic acid as the eluent of several systems tested, this proved to be the only one capable of separating successfully the rhodamine acid from its ester.

Spectra

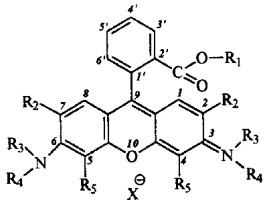
IR spectra was recorded on a Mattson 5000-FTS Fourier transform (FT) IR spectrophotometer and UV–visible (Vis) spectra were obtained with a Perkin-Elmer Lambda 6 instrument.

^{1}H and ^{13}C NMR spectra were recorded with a General Electric QE-PLUS-300 spectrometer equipped with NICOLET and NUTS software.

All chemical shifts were determined on the δ scale relative to internal TMS (=0.00 ppm) for the ^{1}H and to $CDCl_3$ (=77.7 ppm) for the ^{13}C spectra. The spectra were recorded from solutions of a given dye in $CDCl_3$ or $CDCl_3$ containing a drop of DMSO-d_6.

^{1}H NMR and COSY spectra were recorded at room temperature at 300.15 MHz in a 5 mm probe with a 90° pulse width of 12.5 μs and a relaxation delay of 1.0 μs. COSY spectra were processed using a sinusoidal multiplication in both dimensions and recorded in magnitude mode. The final data matrix was symmetrized after multiplication with a sine window function. Typically 256 FIDs were recorded in t_1 of size 1024 and eight scans each.

Table 1. Structures and yields of rhodamine esters



Starting rhodamine	Rhodamine ester	R_1	R_2	R_3	R_4	R_5	X	Yield (%)
B	**1**	Me	H	Et	Et	H	ClO_4	83
	2	Me	H	Et	Et	H	I	79
	3	Me	H	Et	Et	H	Br	94
	4	Et	H	Et	Et	H	ClO_4	95
	5	Et	H	Et	Et	H	I	96
	6	Et	H	Et	Et	H	Br	91
	7	*n*-Pr	H	Et	Et	H	ClO_4	93
	8	*n*-Pr	H	Et	Et	H	I	95
	9	*n*-Pr	H	Et	Et	H	Br	76
	10	*n*-Bu	H	Et	Et	H	ClO_4	90
	11	*n*-Bu	H	Et	Et	H	I	70
	12	*n*-Bu	H	Et	Et	H	Br	72
19	**13**	Me	Me	H	Et	H	ClO_4	98
	14	Et	Me	H	Et	H	ClO_4	97
116	**15**	Me	H	H	Me	H	ClO_4	70
	16	Et	H	H	Me	H	ClO_4	95
110	**17**	Me	H	H	H	H	ClO_4	98
	18	Et	H	H	H	H	ClO_4	98
101	**19**	Me	—$(CH_2)_3$—		—$(CH_2)_3$—		ClO_4	97
	20	Et	—$(CH_2)_3$—		—$(CH_2)_3$—		ClO_4	75

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Table 2. UV–Vis and IR spectral data for rhodamine esters

Rhodamine ester	IR (cm^{-1})[a]	UV–Vis, λ_{max} (nm)[b]
1	1082, 1593, 1728	556
2	1076, 1587, 1722	556
3	1076, 1589, 1722	556
4	1074, 1589, 1709	556
5	1093, 1589, 1714	556
6	1077, 1591, 1715	556
7	1074, 1589, 1709	556
8	1074, 1591, 1707	556
9	1091, 1590, 1715	556
10	1072, 1583, 1707	556
11	1077, 1590, 1716	556
12	1076, 1591, 1717	557
13	1091, 1608, 1721, 3402	529
14	1084, 1606, 1710, 3396	530
15	1092, 1642, 1720, 3325	525
16	1078, 1606, 1712, 3329	528
17	1084, 1595, 1712, 3157	511
18	1094, 1608, 1720, 3306	512
19	1085, 1595, 1720	578
20	1099, 1597, 1714	577

[a] KBr disc.
[b] EtOH–1% DMF.

^{13}C NMR spectra were recorded at room temperature at 75.6 MHz, a pulse width for a 90° pulse of 20.0 μs, a relaxation delay of 1.0 μs and broadband proton decoupling.

Short- and long-distance heteronuclear correlations were made using HETCOR and COLOC type experiments, respectively, at room temperature. These spectra were obtained as matrices of 4096 × 128 and 4096 × 256 blocks of data. Compounds were dissolved in $CDCl_3$ or $CDCl_3$ containing a drop of DMSO-d_6

RESULTS AND DISCUSSION

The structure, numbering scheme and yields obtained for the different rhodamine esters are presented in Table 1. The UV–Vis and FTIR spectra data are given in Table 2 and the ^{1}H and ^{13}C NMR spectral data in Tables 3 and 4 and Tables 5 and 6, respectively.

Generally, the UV–Vis spectra show a 10–15 nm bathochromic shift with respect to the acid rhodamine.

The IR spectra of all esters of the different rhodamines display typically three strong bands at 1072–1094, 1583–1597 and 1707–1728 cm^{-1}, which are characteristic of C—O, C═C and C═O axial deformation modes, respectively.

The 3′/8′ protons and the 4′/5′ protons, responsible for two doublets and two triplets, respectively, were distinguished by the effect of the substituted ester and diphenylmethine on the different positions of the ring known from the literature[5] together with the observation of the roof effect. These attributions were confirmed by one- and multiple-bond homo- and heteronuclear correlation experiments.

Typical values of the *ortho* and *meta* coupling constants were observed in the ester substituted phenylmethine ring, with values of 7.5–8.0 Hz and 1.0–1.5 Hz, respectively. The 1–2/7–8 *ortho* constants and 2–4/5–7 *meta* constants observed for the diphenylmethine rings also present typical values of coupling constants of 9.0–9.5 and 2.0–2.5 Hz, respectively.

Noteworthy is the stronger concentration dependence of the proton signals close to nitrogen with a relative 4,5-proton deshielding and 2,7-proton shielding as the concentration of the sample decreases, leading to an overall better resolution of the spectra.

The almost identical chemical shifts of C-4′ and C-6′ were assigned by long-range correlation. As expected, the chemical shift of the ester carbonyl appears to the lowest field, ca 165 ppm.

The **19** and **20** saturated ring proton and carbon chemical shifts were unequivocally assigned by a combination of direct and long-range

Table 3. ^{1}H NMR aromatic spectral data for rhodamine esters [$CDCl_3$; δ (ppm), J (Hz)]

Rhodamine ester	H-1,8 d (9.0–9.5)	H-2,7 dd (9.0–9.5; 2.0–2.5)	H-4,5 d (2.0–2.5)	H-3′ dd (7.5–8.0; 1.0–1.5)	H-4′ dt (7.5–8.0; 1.0–1.5)	H-5′ dt (7.5–8.0; 1.0–1.5)	H-6′ dd (7.5–8.0; 1.0–1.5)
1	7.06	6.85	6.89	8.30	7.75	7.82	7.32
2	7.03	6.86	6.77	8.27	7.72	7.80	7.29
3	7.00	6.86	6.74	8.24	7.69	7.77	7.25
4	7.09	6.90	6.87	8.30	7.75	7.82	7.31
5	7.11	6.93	6.84	8.32	7.77	7.85	7.34
6	7.10	6.94	6.83	8.31	7.75	7.83	7.31
7	7.08	6.86	6.88	8.29	7.72	7.81	7.32
8	7.08	6.84	6.82	8.30	7.74	7.81	7.31
9	7.09	6.93	6.85	8.30	7.75	7.82	7.31
10	7.08	6.88	6.83	8.29	7.74	7.81	7.32
11	7.09	6.91	6.81	8.29	7.75	7.83	7.32
12	7.10	6.94	6.87	8.28	7.75	7.82	7.31
13	6.80 (s)	—	6.88 (s)	8.32	7.77	7.83	7.29
14	6.74 (s)		6.79 (s)	8.37	7.79	7.82	7.29
15	6.94	6.84	6.67	8.28	7.73	7.80	7.29
16	6.95	6.85	6.66	8.28	7.73	7.79	7.29
17[a]	6.75	6.64	6.65	8.06	7.53	7.59	7.09
18[a]	6.62	6.52	6.53	7.94	7.42	7.47	6.97
19	6.54 (s)	—	—	8.31	7.75	7.81	7.25
20	6.55 (s)	—	—	8.26	7.70	7.78	7.26

[a] $CDCl_3$ + 1 drop of DMSO.

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Table 4. ^{1}H NMR aliphatic spectral data of substituents of rhodamine esters [$CDCl_3$, δ (ppm), J (Hz)]

Rhodamine ester	R_1	R_2	R_3	R_4	R_5
1	3.69, s	—		1.33, t, 7.0; 3.62; q, 7.0	—
2	3.65, s	—		1.30, t, 7.0; 3.61, q, 7.0	—
3	3.62, s	—		1.27, t, 7.0; 3.59, q, 7.0	—
4	1.07, t, 7.0; 4.07, q, 7.0	—		1.33, t, 7.0; 3.64, q, 7.0	
5	1.10, t, 7.0; 4.10, q, 7.0	—		1.36, t, 7.0; 3.68, q, 7.0	—
6	1.09, t, 7.0; 4.08, q, 7.0	—		1.34, t, 7.0; 3.67, q, 7.0	—
7	0.78, t, 7.0; 1.47, sext., 7.0; 3.98, t, 6.5	—		1.35, t, 7.0; 3.63, q, 7.0	—
8	0.78, t, 7.5; 1.47, sext., 7.0; 3.98, t, 6.5	—		1.32, t, 7.0; 3.63, q, 7.0	—
9	0.79, t, 7.0; 1.45, sext., 7.0; 3.99 t, 6.5	—		1.33, t, 7.0; 3.68, q, 7.0	—
10	0.80, t, 7.5; 1.14, sext., 7.5; 1.40, qt, 7.0; 4.01, t, 7.0	—		1.33, t, 7.0; 3.63, q, 7.0	—
11	0.80, t, 7.5; 1.16, sext., 7.5; 1.42, qt, 7.5; 4.02, t, 7.5	—		1.34, t, 7.0; 3.66, q, 7.0	—
12	0.81, t, 7.5; 1.16, sext., 7.5; 1.40, qt, 7.0; 4.02, t, 6.5	—		1.34, t, 7.0; 3.66, q, 7.0	—
13	3.65, s	2.22, s	5.43, sl	1.43, t, 7.0; 3.56, q, 7.0	—
14	1.00, t, 7.0; 4.05, q, 7.0	2.20, s	5.20, sl	1.43, t, 7.0; 3.53, q, 7.0	—
15	3.65, s	—	NH not detectable	3.04, s	—
16	1.01, t, 7.0; 4.03, q, 7.0	—	NH not detectable	3.04, s	—
17[a]	3.42, s	—		4.17, sl	—
18[a]	0.75, t, 7.0; 3.69, q, 7.0	—		4.99, sl	—
19	3.70, s	3.54, t, 6.9 [NCH_2(CH$_2$)$_2$]; 3.06, t, 6.0 [N(CH$_2$)$_2$CH_2]; 2.13, qt, 6.0 (NCH$_2$CH_2CH$_2$)		3.50, t, 6.0 [NCH_2(CH$_2$)$_2$]; 2.68, t, 6.0 [N(CH$_2$)$_2$CH_2]; 1.98, qt, 6.0 (NCH$_2$CH_2CH$_2$)	
20	1.07, t, 7.0; 4.08, q, 7.0	3.55, t, 6.0 [NCH_2(CH$_2$)$_2$]; 3.05, t, 6.0 [N(CH$_2$)$_2$CH_2]; 2.12, qt, 6.0 (NCH$_2$CH_2CH$_2$)		3.49, t, 6.0 [NCH_2(CH$_2$)$_2$]; 2.66, t, 6.0 [N(CH$_2$)$_2$CH_2]; 1.97, qt, 6.0 (NCH$_2$CH_2CH$_2$)	

[a] $CDCl_3$ + 1 drop of DMSO.

Table 5. ^{13}C NMR spectral data for Rhodamine esters **1–10** [$CDCl_3$; δ (ppm)]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C-1/8	131.3	131.2	131.1	131.2	131.2	131.2	130.3	131.2	131.2	131.2
C-2/7	114.9	114.4	114.3	114.5	114.2	114.3	114.3	114.1	114.3	114.2
C-3/6	154.9	155.8	155.7	155.4	155.4	155.4	155.7	155.5	155.4	155.5
C-4/5	97.4	96.6	96.4	97.0	96.3	96.3	96.8	96.3	96.5	96.3
C-4a/5a	157.5	157.9	157.8	157.7	157.6	157.6	157.9	157.7	157.7	157.7
C-8a/9a	114.5	113.7	113.6	114.1	113.5	113.5	113.9	113.5	113.6	113.4
C-9	158.8	158.9	158.7	158.9	158.9	158.9	158.9	158.8	158.8	158.7
C-1′	133.4	133.5	133.5	133.2	133.3	133.3	133.3	133.3	133.4	133.3
C-2′	129.7	130.3	130.2	130.3	130.3	130.3	130.6	130.2	130.3	130.2
C-3′	131.3	131.3	131.1	131.1	131.4	131.2	130.2	131.3	131.2	131.2
C-4′	130.2	130.3	130.1	130.1	130.1	130.0	130.1	130.1	130.1	130.1
C-5′	133.1	132.9	132.8	132.7	133.0	132.9	132.7	132.9	132.9	132.9
C-6′	130.5	130.3	130.1	130.2	130.1	130.1	130.1	130.3	130.3	130.3
C═O	165.5	165.3	165.2	164.9	165.0	164.9	165.1	165.1	165.1	165.2
OR_1	55.0	52.3	52.2	61.3 13.6	61.5 13.8	61.4 13.8	67.1 21.6 9.9	67.1 21.6 10.1	67.2 21.6 10.2	65.5 30.3 19.0 13.5
NR_3	46.7	46.2	46.0	46.2	46.2	46.2	46.1	46.0	46.2	46.0
NR_4	12.4	12.7	12.6	12.4	12.7	12.6	12.4	12.5	12.6	12.5

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Table 6. ^{13}C NMR spectral data for rhodamine esters **11–20** [$CDCl_3$; δ (ppm)]

	11	**12**	**13**	**14**	**15**	**16**	**17**[a]	**18**[a]	**19**	**20**
C-1/8	131.2	131.2	128.9	128.7	131.1	131.1	131.1	131.1	125.7	125.9
C-2/7	114.5	114.4	126.7	125.6	117.2	116.9	117.3	117.4	123.6	123.8
C-3/6	155.8	155.4	154.8	156.2	158.1	158.1	158.0	157.8	151.0	151.3
C-4/5	96.6	96.9	95.6	93.9	94.8	94.6	98.1	97.8	105.1	105.5
C-4a/5a	157.8	157.6	156.9	157.3	158.4	158.5	159.3	159.3	152.0	152.2
C-8a/9a	113.7	113.7	115.0	113.7	113.6	113.6	113.7	113.5	112.7	113.1
C-9	158.9	158.7	157.8	158.0	159.0	158.9	159.3	159.3	155.9	155.8
C-1′	133.2	133.2	133.8	133.6	133.7	133.4	133.5	133.6	132.8	134.5
C-2′	130.2	130.7	129.7	130.5	129.8	130.1	130.2	130.4	129.6	130.5
C-3′	131.2	131.3	131.3	131.1	130.0	129.9	130.9	130.8	129.9	131.0
C-4′	130.2	130.1	130.1	130.0	130.2	130.1	129.9	129.8	130.0	129.9
C-5′	132.7	132.9	133.1	132.5	132.8	132.6	132.4	133.3	131.1	132.8
C-6′	130.2	130.3	130.4	130.1	130.2	130.2	130.0	129.9	130.3	130.7
C═O	165.0	165.1	162.2	164.9	165.4	164.8	165.1	165.6	164.1	165.3
OR_1	65.3 30.3 18.8 13.2	65.4 30.3 18.9 13.5	52.2	61.2 13.4	52.2	61.3 13.6	52.0	61.0 13.3	52.4	61.4 13.9
R_2	—	—	17.3	17.1	—	—	—	—	50.8[b]	51.0[b]
NR_3	46.2 12.6	46.2 12.5	39.8 13.4	38.6 13.6	30.0 —	30.0 —	— —	— —	20.4[c] 27.5[d]	20.7[c] 27.7[d]
NR_4	$=NR_3$	$=NR_3$	$=NR_3$	$=NR_3$	$=NR_3$	$=NR_3$	—	—	50.3[b] 19.5[c]	50.6[b] 19.8[c]
R_5	—	—	—	—	—	—	—	—	19.8[d]	20.0[d]

[a] $CDCl_3$ + 1 drop of DMSO.
[b] $NCH_2CH_2CH_2$.
[c] $NCH_2CH_2CH_2$.
[d] $NCH_2CH_2CH_2$.

heteronuclear correlation, starting from the H-1/H-8 cross peak and the methylene signal in the benzylic position of R_2.

The assignment of proton signals of the different aliphatic groups (R^1, R^2, R^3, R^4 and R^5) was easily and unambiguously achieved by the analysis of the multiplicity and relative integration of the signals and by the shielding effect known from literature data.[5] The assignment of the related carbon was mainly achieved based on typical δ_c data[5] and by the observation of the strong signals of the *N*-alkyl groups of the weaker ester group signal(s). These assignments were also confirmed by homo- and heteronuclear one- and multiple-bond correlation experiments.

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