# Merocyanines Derived from Substituted 4-Hydroxycoumarins. Part II. Determination of Relative Acidity

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The relative acidity of different 4-hydroxycoumarins has been determined by two methods: (i) by extension of the application of Forster's rule to the absorption data of p-dialkylaminobenzylidene derivatives of different 4-hydroxycoumarins and their aza analogues, (ii) by the application of Brooker's deviation factor. For evaluation by the second method, the absorption data of oxonols of different 4-hydroxycoumarins have been collected.

In the present communication, 4-hydroxycoumarins derived from phenol, resorcinol, and ∝- and β-naphthols have been prepared and their relative acidity has been determined by a method involving the application of Forster's rule[1] and also by application of Brooker's deviation factor[2]

In the method involving Forster's absorption rule, absorption data of p-dialkylaminobenzylidene derivatives and the corresponding aza analogues of 4-hydroxycoumarins have been considered. The dialkylaminobenzylidene derivatives and their aza analogues have the general structure, shown below:

(I: X=CH and X=N)
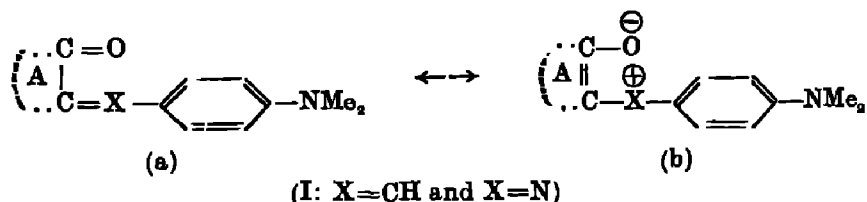
The nucleus A, which is the acidic one, has been varied and different acidic nuclei used are chroman-2,4-dione, 7-hydroxychroman-2,4-dione, 5,6-benzochroman-2,4-dione, and 7,8-benzochroman-2,4-dione. These compounds were prepared by condensing the corresponding chroman-2,4-diones with dimethylaminobenzaldehyde (X=CH) and with p-nitrosodimethylaniline (X=N).

In these compounds, the most likely excited structure involve -$\overset{\oplus}{X}$- and not -$\overset{\ominus}{X}$- and the replacement of X=CH by X=N results in a bathochromic shift. This was expected on the basis of Forster's rule, which states that the absorption maximum will increase with the decreasing tendency of the characteristic charge being retained in the chromophoric chain. In the above case, the positive charge in -$\overset{\oplus}{N}$- will be retained relatively with greater difficulty than the positive change in -$\overset{\oplus}{CH}$-. Hence the aza analogues (X=N)

1. Z. Elektrochem., 1939, 45, 548.
2. J. Amer. Chem. Soc., 1951, 73, 5532.

are expected to absorb at a higher wave length than the corresponding dialkylaminostyryl dyes (X=CH).

The significance of structure (b) will increase with increasing acidity, i.e. electron-attracting property of the nucleus A, so that a larger bathochromic shift will be observed in a compound derived from a more acidic nucleus.
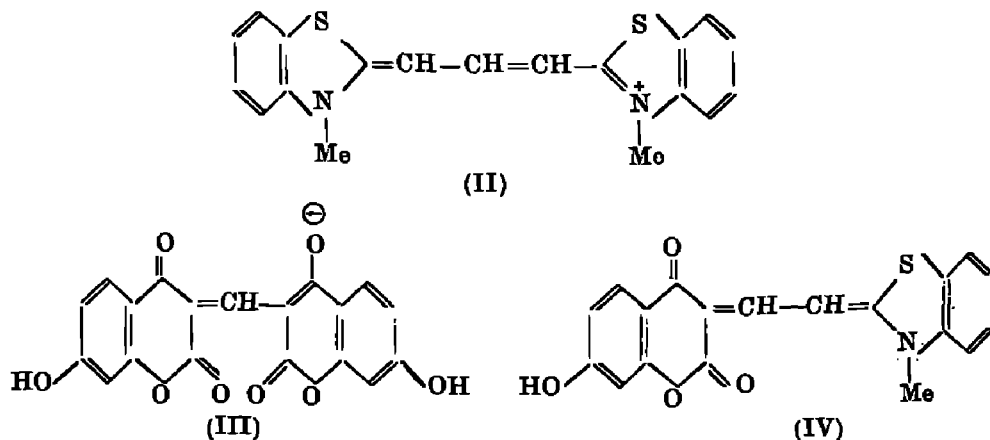
TABLE I

Nucleus A.	Absorption maxima (mμ).		Shift (mμ).	
	X = CH.	X = N.	Expected.	Obs.
1 Chroman-2,4-dione	505	540	Bathochromic	35
2 7-Hydroxychroman-2,4-dione	505	543	,,	38
3 5,6-Benzochroman-2,4-dione	510	540	,,	30
4 7,8-Benzochroman-2,4-dione	510	540	,,	30

*Vide structure (I).

The data in the above table show that the bathochromic shifts for the replacement of =CH-by = N - for the dialkylaminobenzylidene derivatives and the corresponding aza analogues of chroman-2.4-dione. 7-hydroxychroman-2,4-dione, 5,6-benzochroman-2,4-dione, and 7,8-benzochroman-2.4-dione are 35. 38, 30, and 30mμ respectively. Hence the relative acidity is in the following order : 5,6- and 7,8-benzochroman-2,4-dione > chroman-2,4-dione > 7-hydroxychroman-2,4-dione.

The relative acidity of the corresponding chroman-2,4-diones has also been evaluated with the help of "Deviation factor". Brooker[a] has postulated that in a series of merocyanines containing the same basic nucleus, the deviation will be highest for the least acidic nucleus and as the acidity is increased, the deviation is correspondingly decreased. Deviation is considered as the difference between the absorption maximum of the corresponding symmetrical cyanine and oxonol. Deviation is calculated as illustrated here by taking the case of the merocyanines (IV) derived from 2-methylbenzothiazole and the acidic nucleus, 7-hydroxychroman-2,4-dione. The absorption maximum of the symmetrical trimethin cyanine derived from 2-methylbenzothiazole (II) is 565 mμ and that of the monomethin oxonol derived from 4,7-dihydroxycoumarin (III) is 450 mμ. The dimethin merocyanine (IV), composed of both the nuclei, however, absorbs at 490 mμ. Deviation is therefore 17.5 mμ.

(II)

(III)   (IV)

Table II shows that the deviation of merocyanines derived from 2-methylbenzothiazole and different 4-hydroxycoumarins derived from phenol, resorcinol, and α- and β-naphthols are 7.5, 17.5, 0.5, and 2.5 mμ respectively, indicating the following order of relative acidity; 5,6- and 7,8-benzochroman-2,4-diones > chroman-2,4-dione > 7-hydroxychroman-2,4-dione.

TABLE II

Deviation of merocyanines.

$$\left(\begin{array}{c} -N.CH_3 \qquad O=C \\ A \mid \qquad\qquad\quad \mid \quad B \\ -C =(CH—CH=)_nC—C \\ \qquad\qquad\qquad\qquad \parallel \\ \qquad\qquad\qquad\qquad O \end{array} \right)$$

Nucleus B (-2,4-diones).	n.	Absorption maxima.			λ_{max} (calc.).	Deviation·
		Symm. oxonol.	Symm. cyanine.	Merocyanine.		
Nucleus A = Benzothiazole.						
Chroman-	1	430 mμ	565 mμ	490 mμ	497.5 mμ	7.5 mμ
	2	520	660	584	594.5	10.5
	3	622	760	670	691.0	21.0
7-Hydroxychroman-	1	450	565	490	507.5	17.5
	2	550	660	584	605.0	25.0
	3	650	760	680	705.0	25.0
5,6-Benzochroman-	1	430	565	495	497.5	2.5
	2	540	660	600	600.0	0.0
	3	640	760	687	700.0	13.0
7,8-Benzochroman-	1	440	565	502	502.5	0.5
	2	539	660	600	599.5	—0.5
	3	634	760	684	697.0	13.0
Nucleus A = Benzoxazole.						
Chroman-	3	622	680	627	651.0	24.0
7-Hydroxychroman-	3	650	680	624	665.0	41.0
5,6-Benzochroman-	3	640	680	646	660.0	14.0
7,8-Benzochroman	3	634	680	645	657.4	12.0
Nucleus A = Quinoline-2.						
Chroman-	2	529	710	592	619.5	27.5
7-Hydroxychroman-	2	550	710	597	630.0	33.0
5,6-Benzochroman-	2	540	710	602	625.0	23.0
7,8-Benzochroman-	2	539	710	598	624.5	26.5

The same conclusions are also arrived at by considering the absorption of merodicarbo ($n=2$) and merotricarbo ($n=3$) cyanines derived from 2-methylbenzothiazole as the fixed basic nucleus and varying acidic nuclei like chroman-2,4-dione, 7-hydroxychroman-2,4-dione, 5,6-benzo- and 7,8-benzo-chroman-2,4-diones.

The absorption data of oxonols are necessary for calculating the deviation. The mono-, tri-, and penta-methin oxonols were prepared by reaction with ethyl orthoformate, β-anilinoacrolein-anil hydrochloride, and glutaconic aldehyde dianilide hydrochloride respectively. Their preparations are described in the Experimental. The experimental procedure for preparations of the merocyanines, deviations of which are considered, has been described in Part I[3].
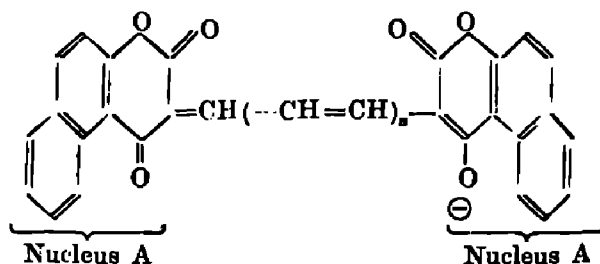
3. This *issue*, p. 797.

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EXPERIMENTAL

Bis-[3-(*5,6-benzochroman-2,4-dione*)] *methin Oxonol.*—5,6-Benzochroman-2,4-dione (0.48 g., 2*M*) and triethyl orthoformate (0.15 g., 1*M*) were boiled for 3 min. in acetic anhydride (5 ml) in presence of triethylamine (4 drops). After removal of excess of the solvent, addition of ether separated the desired product. Solid, thus obtained, was washed with ethanol and finally recrystallised from the same solvent, m.p. 204° (decomp.), yield 46%. (Found: C, 73.96; H, 3.10. $C_{27}H_{14}O_6$ requires C, 74.64; H, 3.22%).

Bis-[3-(*5,6-benzochroman-2,4-dione*)] *trimethin Oxonol.* — 5,6-Benzochroman-,2,4-dione (0.48 g., 2*M*) and β-anilinoacrolein-anil hydrochloride (0.26 g., 1*M*) were refluxed in acetic anhydride (5 ml) in presence of triethylamine (4 drops) for 5min. After removal of excess of solvent, the desired product separated on addition of ether. It was washed with water, followed by ethanol, and finally crystallised from ethanol; m.p. above 3C0°, yield 51%. (Found: C, 74.88; H, 3.28. $C_{29}H_{16}O_6$ requires C, 75.37; H, 3.47%).

TABLE III

$$=CH(-CH=CH)_n-$$

Nucleus A   Nucleus A

Nucleus A (-2,4-diones).	n.	M.P.	%Yield.	λ max.	Found.		Reqd.
Chroman-	1	178°(d)	44	529 mμ	C : 68.04%		70.00%
					H : 3.12		3.33
,,	2	146°	68	622	C : 70.86		71.40
					H : 3.36		3.62
5,6-Benzochroman-	0	204°(d)	46	430	C : 73.96		74.64
					H : 3.10		3.22
,,	1	>300°	51	540	C : 74.88		75.37
					H : 3.28		3.47
,,	2	>300°	49	640	C : 75.89		76.24
					H : 3.32		3.69
7,8-Benzochroman-	1	>305°	54	539	C : 75.21		75.37
					H : 3.31		3.47
,,	2	276°(d)	58	634	C : 75.69		76.24
					H : 3.44		3.69
7-Hydroxychroman-	0	98°	47	450	C : 61.79		62.16
					H : 2.66		2.73
,,	1	161°	52	550	C : 62.88		64.26
					H : 2.74		3.05
,,	2	210°	58	650	C : 64.69		65.81
					H : 3.06		3.34

N.B.—*d* denotes decomposition·

Bis-[3-(*5,6-benzochroman-2,4-dione*)] *pentamethin Oxonol.*—5,6-Benzochroman-2,4-dione (0.5 g.) and glutaconic aldehyde dianilide hydrochloride (0.3 g.) were heated together with triethylamine (0.2ml) in acetic anhydride (8 ml) for 6 min. Excess of the solvent was

removed and ether was added when the desired product separated. It was filtered, washed with water, followed by dilute ethanol, and finally crystallised from ethanol; m.p. above 300°, yield 49%. (Found: C, 75.89; H, 3.32. $C_{31}H_{18}O_6$ requires C, 76.24; H, 3.69%).

The analytical data of all the above compounds and their related derivatives are recorded in Table III.

3-p - *Dimethylaminobenzylidene*-7 - *hydroxychroman*-2,4 - *dione*. — 4,7-Dihydroxycoumarin (0.18 g., 1M) and p-dimethylaminobenzaldehyde (0.15 g., 1M) were heated in acetic anhydride (6 ml) for 10 min. in presence of sodium acetate (0.2 g.). Excess of the solvent was removed under reduced pressure and chilled when crystals appeared. The solid, thus obtained, was filtered, washed with water, and finally recrystallised from ethanol; m.p. 198°, yield 70%. (Found: C, 69.50; H, 4.84. $C_{18}H_{16}O_4N$ requires C, 69.64; H, 5.14%).

Aza Analogue of 3-p-*Dimethylaminobenzylidene*-7-*hydroxychroman*-2,4-*dione*.—4,7-Dihydroxycoumarin(0.18g., 1M) and p-nitrosodimethylaniline (0.15 g., 1M) were heated in acetic anhydride (6 ml) on a sand bath for 45 min. The solvent was removed under reduced pressure and the resulting gum was washed several times with HCl (dil.). The dye, thus obtained, was crystallised from ethanol; yield 68%, m.p. 92°. (Found: C, 65.11; H, 4.95; N, 8.86. $C_{17}H_{16}O_4N_2$ requires C, 65.34; H, 4.82; N, 8.99%).

The analytical data of all the above compounds are recorded in Tables IV and V.

TABLE IV
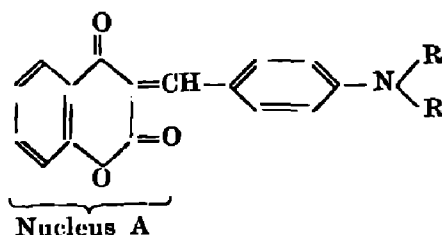
Nucleus A

Nucleus A.	Nature of R.	M.P.	%Yield.	λ_{max}.	Found.		Reqd.
Chroman-2,4-dione	Me	200°	60	505mμ	C :	73.14%	73.52%
					H :	4.86	5.12
Chroman-2,4-dione	Et	168°(d)	54	507	C :	73.11	73.35
					H :	5.56	5.90
7-Hydroxychroman-2,4-dione	Me	198°	70	505	C :	69.50	69.64
					H :	4.84	5.14
,,	Et	246°	65	507	C :	70.89	71.14
					H :	4.86	5.36
5,6-Benzochroman-2,4-dione	Me	235°	55	510	C :	77.48	77.80
					H :	5.30	5.19
,,	Et	162°	45	510	C :	78.88	79.03
					H :	6.13	6.39
7,8-Benzochroman-2,4-dione	Me	199°	51	510	C :	77.52	77.80
					H :	4.89	5.19
,,	Et	167°	49	510	C :	78.73	79.03
					H :	6.16	6.39

TABLE V
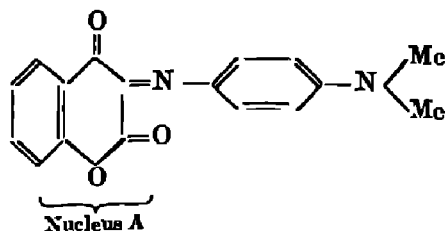
Nucleus A

Nucleus A.	M.P.	%Yield.	λ_{max}.	Found.		Reqd.
Chroman-2,4-dione	96°(d)	50	540 mμ	C :	68.96%	69.29%
				H :	4.61	4.74
				N :	9.32	9.48
7-Hydroxychroman-2,4-dione	92°	68	543	C :	65.11	65.34
				H :	4.95	4.52
				N :	8.86	8.99
5,6-Benzochroman-2,4-dione	186°	58	540	C :	72.68	72.73
				H :	5.24	5.20
				N :	7.89	8.08
7,8-Benzochroman-2,4-dione	150°	53	540	C :	72.59	72.73
				H :	4.92	5.20
				N :	7.89	8.08

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