A New Class of Laser Dyes from Acridinedione Derivatives

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Synthesis of 10-aryl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione as a new class of laser dyes is reported. These dyes lase around 475-495 nm and are compared to the standard dye coumarin 102.

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Since the observation of laser action from organic compounds many classes of dyes have been demonstrated to give laser action [1]. Several new compounds have been synthesised and investigated in order to get high laser efficiency, wide tunability and photostability [2-4]. With this in mind, we have synthesised a new class of laser dyes belonging to the acridinediones family [5,6]. All these dyes lase around 475-495 nm under Nitrogen and Nd-YAG excitation and their laser characteristics are comparable with the coumarin 102.

Herein we report the synthesis of the desired acridinediones and their laser properties. Condensation of cyclohexane-1,3-dione with aldehydes furnished the tetraketone 1, which on reaction with aromatic amines (under different conditions) afforded the acridinediones 2-4 (Scheme 1). The acridinediones 2,3,4 were characterised by ir, nmr, ms and elemental analysis. The 'H nmr spectra of all the acridinediones in general showed the characteristic signals for the C2 and C7, C3 and C6, C4 and C5 and C9 pro-

1 +
$$A_r-NH_2$$
 $\xrightarrow{(ii)}$ R A_r R

R = H, R' = Subst. $R = CH_3, R' = H$

i. aq. MeOH/\(\Delta\); ii. a. EtOH/P2O5/r.t. stirring (for 2a-k, 3a-e) b. AcOH/ Δ (for 3 f-h) c.. EtOH/AcOH/ Δ (for 2l) d.. EtOH/P₂O₅/ Δ (for 4a-e)

tons. The two protons of C₂ exhibited geminal coupling in compounds 2g and 2j. The spectra of 4d and 4e exhibited the difference between the quasi-axial and quasi-equatorial protons of C₄ and C₅. The mass spectra of the acridinediones in general showed the molecular ion signal as the base peak while the other fragmentation peaks were less than 10% intensity. For compounds 3a-c,e, the parent ions were >3%, while the (M*-R') signal constituted the base peak.

Antaki [7] reported the condensation of 2,2'-arylidenebis(cyclohexane-1,3-diketone) with aromatic amines giving very low yields of acridinediones. The above procedure was modified to obtain the products 2 in good yields. When 2,2'-arylidenebis(cyclohexane-1,3-diketone) and arylamine (5 mmoles each) were refluxed in acetic acid (100 ml), only a trace amount of acridinedione was isolated, while the major product was dioxoxanthene [8]. But when it was refluxed with 10 ml of acetic acid, a good yield of acridinedione was obtained. Thus the dilution increases only the self-condensation of enolic OH groups leading to the formation of dioxoxanthenes.

Mel'nik et al. [9] reported the synthesis of acridinediones from dimedone in very poor yields (2-20%), which was also modified to get 75-85% yields.

Next we studied the laser properties of all the acridinediones synthesised in the present work. Except 9-aryl substituted acridinediones, all compounds showed good fluorescence in organic solvents. The laser yields of the acridinediones are shown in the Table 2. The laser yield is reported in percentage in comparison with the standard laser dye coumarin-102, which also lases around the lasing wavelengths of the acridinediones.

EXPERIMENTAL

Melting points were uncorrected. The ir spectrum were recorded in Perkin-Elmer 258 spectrophotometer in potassium bromide discs. The 'H-nmr spectra were recorded on a Varian EM 390 spectrometer. Mass spectra were recorded on Shimatzu QP 1000 and Hewlett Packard 5985 GC/MS. Laser studies were performed by Nitrogen laser and Quanta DCR 2 Nd-YAG laser instruments. Chromatographic purifications were performed on silica gel (100-200 mesh).

Table 1

				Table 1				
Compound Molecular formula	Yield %	Mp °C	IR Cm ⁻¹	NMR CDCl ₃ /DMSO-d ₆ /TMS	MS M+		Analysis cd./Fou H	
$\mathbf{2a}$ 10-(4-methylphenyl) $C_{20}H_{21}NO_2$	78	260 dec	1640, 1580	1.8 (m, 8H, =C-CH ₂ -CH ₂ -), 2.25 (m, 7H, CO-CH ₂ , Ar-CH ₃), 3.1 (s, 2H, = C-CH ₂ -C=), 7.05-7.35 (AB q, 4-H, Ar-H), ¹³ C nmr: 18.7 (3.6), 21.1 (Ar-CH ₃), 21.4 (4.5), 28.2 (2.7), 36.3 (9), 111.9 (8a, 9a), 129.4, 130.4, 136.6, 139.3 (Ar), 153.0 (10a, 4a), 196.7 (CO, 1, 8)	307	78.14 78.21		
b 10-(phenyl) C ₁₉ H ₁₉ NO ₂	68	245 dec	1640, 1580	1.8 (m, 8H, = C-CH ₂ -CH ₂ -), 2.25 (m, 4H, - (CO-CH ₂), 3.2 (s, 2H, =C-CH ₂ -C=), 7.0-7.4 (m, 5H, Ar-H), ¹³ C nmr: 18.7 (3,6), 21.4 (4,5), 28.0 (2,7), 36.3 (9), 111.7 (8a 9a), 114.6, 129.0, 129.7, 139.1 (Ar), 152.7 (10a,4a), 196.6 (CO, 1, 8)	-		6.52 6.38	
c 10-(4-chlorophenyl) C ₁₉ H ₁₈ NO ₂ Cl	67	234 dec	1640, 1580	1.93 (m, 8H, = C-CH ₂ -CH ₂ -), 2.27 (m, 4H, CO-CH ₂), 3.1 (s, 2H, =C-CH ₂ -C=), 7.0-7.47 (AB q, 4H, Ar-H), ¹³ C nmr: 18.7 (3,6), 21.3 (4,5), 28.1 (2,7), 36.2 (9), 112.0 (8a, 9a), 129.9, 131.2, 135.1, 137.7 (Ar), 153.3 (10a, 4a), 196.6 (CO, 1, 8)	327, (329)	69.61 69.35	5.53 5.53	4.27 4.09
d 10-(4-methoxyphenyl) C ₂₀ H ₂₁ NO ₃	74	240 dec	1640, 1580	1.9 (m, 8H, = C-CH ₂ -CH ₂ -), 2.3 (m, 4H, -CO-CH ₂), 3.15 (s, 2H, =C-CH ₂ -C=), 3.8 (s, 3H, -OCH ₃), 6.8-7.1 (AB q, 4H, Ar-H), 13C nmr: 18.9 (3,6), 21.5 (4,5), 36.4 (9), 55 (-OCH ₃), 112.0 (8a, 9a), 114.9, 130.8, 131.9, 159.9 (Ar), 153.4 (10, 4a), 196.8 (CO, 1, 8)	323		6.54 6.39	
e 10-(4-methylphenyl) $C_{20}H_{21}NO_2$	71	242 dec	1640, 1580	2.0 (m, 8H, = C-CH ₂ -CH ₂ -), 2.37 (m, 7H, CO-CH ₂ , Ar-CH ₃), 3.3 (s, 2H, =C-CH ₂ -C=), 7.0-7.45 (m, 4H, Ar-H), ¹³ C nmr: 17.6 (3,6), 19.0 (-CH ₃), 27.6 (2,7), 21.6 (4,5), 36.5 (9), 112.2 (8a, 9a), 127.5, 129.6, 130.0, 131.5, 137.3, 138.2 (Ar), 152.5 (10a, 4a), 196.7 (CO, 1, 8)	307 (100%)	78.14 77.91	6.88 6.61	4.55 4.32
f 10-(4- N - N -dimethylaminophenyl) $C_{21}H_{24}N_2O_2$	75	246 dec	1640, 1580	1.6 (m, 8H, = C-CH ₂ -CH ₂ -), 2.16 (m, 4H, -CO-CH ₂ -), 2.42 (s, 6H, -N(CH ₃) ₂), 3.0 (s, 2H, =C-CH ₂ -C=), 6.6-7.2 (AB q, 4H, Ar-H), ¹³ C nmr: 18.8 (3,6), 21.5 (4,5), 28.1 (2,7), 36.4 (9), 40.4 (N-CH ₃), 111.6 (8a, 9a), 112.2, 127.4, 130.0, 150.3 (Ar), 154.1 (10a, 4a), 196.7 (CO, 1, 8)	-		7.19 7.06	
g 10-(2-chloro-6- methylphenyl C ₂₀ H ₂₀ NO ₂ Cl	75	258-260	1620, 1580	1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.3 (m, 7H, -CO-CH ₂ -, ArCH ₃), 3.0-3.6 (q, 2H, =C-CH ₂ -C=), (J _{gem} = 20 Hz), 7.3-7.5 (m, 3H, Ar-H)	-	70.27 70.17	5.89 5.67	4.09 4.19
h 10-(4-nitrophenyl) C ₁₉ H ₁₈ N ₂ O ₄	72	208-210	1630, 1580 1510, 1340	1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.2-2.5 (m, 4H, -CO-CH ₂ -), 3.2 (s, 2H, =C-CH ₂ -C=), 7.6 & 8.5 (AB q, 4H, Ar-H), (J = 7.5 Hz)	338 (100%)		5.36 5.21	
i 10-(4-nitrophenyl) C ₁₉ H ₁₈ N ₂ O ₄	66	234-236	1640, 1590 1520, 1340	1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.2-2.5 (m, 4H, -CO-CH ₂ -), 3.2 (s, 2H, =C-CH ₂ -C=), 7.5-8.4 (m, 4H, Ar-H)	338 (100%)		5.36 5.21	
j 10-(2,4-dimethyl- 6-bromophenyl) C ₂₁ H ₂₂ NO ₂ Br	76	278-280	1620, 1580	1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 1.9-2.3 (m, 10H, -CO-CH ₂ , Ar-CH ₃), 2.9-3.3 (q, 2H, =C-CH ₂ -C=), (J _{gem} = 20 Hz), 7.15 & 7.35 (bs, 2H, Ar-H)	-		5.53 5.13	
k 10-(α-naphthyl) C ₂₃ H ₂₁ NO ₂	75	232-234	1640, 1610 1590	1.6-1.95 (m, 8H, = C-CH ₂ -CH ₂ -), 2.2-2.4 (t, 4H, -CO-CH ₂), 3.35 (s, 2H, =C-CH ₂ -C=), 7.3-8.1 (m, 7H, År-H)	343 (100%)	80.44 80.16	6.16 5.82	4.07
l 10-(p-terphenyl) C ₃₁ H ₂₇ NO ₂	66	240-242	1630, 1590 1580	1.9-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.3 (t, 4H, -CO-CH ₂ -), 3.2 (s, 2H, =C-CH ₂ -C=), 7.15-7.7 (m, 13H, Ar-H)	445 (100%)		6.10 5.91	
3a 9-methyl-10-(4- methylphenyl) C ₂₁ H ₂₃ NO ₂	77	240-242	1640, 1580	1.05 (d, 3H, = C-CH-), (J = 7.5 Hz), 1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.2-2.4 (m, 7H, -CO-CH ₂ , Ar-CH ₃), 4.2 (q, 1H, =C-CH-C=), 7.1-7.5 (AB q, 4H, Ar-H), (J = 7.5 Hz)	321 (4%) 306 (M+-CH ₃) (100%)		7.21 7.41	

Table 1 (continued)

				Table 1 (continued)				
Compound Molecular formula	Yield %	Mp °C	IR Cm ⁻¹	NMR CDC1 ₃ /DMSO-d ₆ /TMS δ	MS M+	Analysis Calcd./Found C H N		und
				CH ₃				
b 9-methyl-10-(4- chlorophenyl) C ₂₀ H ₂₀ NO ₂ Cl	79	238-240	1640, 1580	1.05 (d, 3H, = C-CH-C=), 1.8-2.05 (m, 8H, = C-CH ₂ -CH ₂ -), 2.25-2.4 (m, 4H, -CO-CH ₂ -), 4.2 (q, 1H, =C-CH-C=), 7.10-7.6 (AB q, 4H, Ar-H)	341 (2%) 326, (M+-CH ₃) (100%)	70.27 70.73	5.89 5.89	4.09 4.08
				CH ₃				
c 9-methyl-10-(2- methylphenyl) C ₂₁ H ₂₃ NO ₂	76	228-230	1640, 1580	1.0 (d, 3H, =C-C-H=), J = 7.5 Hz, 1.8-2.1 (m, 8H, = C-CH ₂ -CH ₂ -), 2.2-2.5 (m, 7H, -CO-CH ₂ -, Ar-CH ₃), 4.1 (q, 1H, =C-CH-C=), 7.1-7.4 (m, 4H, Ar-H)	321 (2%) 306 (M+-CH ₃) (100%)	78.47 78.34		4.35 4.23
d 9-propyl-10-(4- methylphenyl) C ₂₃ H ₂₇ NO ₂	79	164-166	1640, 1580	0.8-1.4 (m, 7H, CH ₂ -CH ₂ -CH ₃), 1.8-2.4 (m, 15H, =C-CH ₂ -CH ₂ -CH ₂ CO, Ar-CH ₃), 4.15 (q, 1H, =C-CH-C=), 7.1-7.46 (AB q, 4H, Ar-H), (J = 7.5 Hz)		78.47 78.27		4.35 4.28
e 9-propyl-10-(4- chlorophenyl) C ₂₂ H ₂₄ NO ₂ Cl	78	168-170	1640, 1580	0.8-1.4 (m, 7H, -CH ₂ -CH ₂ -CH ₃), 1.8-2.4 (m, 12H, =C-CH ₂ -CH ₂ -CH ₂ CO), 4.2 (t, 1H, =C-CH-C=), 7.10-7.45 (AB q, 4H, Ar-H), (J = 7.5 Hz)	326 (M+ -C ₃ H ₇) (100%)	71.23 70.87	6.54 6.45	3.77 4.15
f 9-(2-chlorophenyl)- 1-(4-methylphenyl) C ₂₆ H ₂₄ NO ₂ Cl	74	250-252	1630, 1570	1.8-2.7 (m, 15H, =C-CH ₂ -CH ₂ -CH ₂ -CO, Ar-CH ₃), 5.45 (s, 1H, =C-CH-C=), 7.1-7.8 (m, 8H, Ar-H)	-	74.72 74.70		3.35 3.41
g 9-phenyl-10-(4- methylphenyl) C ₂₆ H ₂₅ NO ₂	77	240-242	1630, 1570	1.8-2.5 (m, 15H, =C-CH ₂ -CH ₂ -CH ₂ CO, Ar-CH ₃), 5.45 (1H, =C-CH-C=), 7.25-7.5 (m, 9H, Ar-H)	-	81.43 81.23		3.65 3.56
h 9-benzyl-10-(4- methylphenyl) C ₂₇ H ₂₇ NO ₂	73	278-280	1640, 1600 1580	1.9-2.1 (m, 8H, =C-CH ₂ -CH ₂ -), 2.3 (m, 7H, CO-CH ₂ -, Ar-CH ₃), 2.75 (d, 2H, CH ₂ -\$\phi\$), 4.5 (t, 1H, =C-CH-C=), 6.9-7.3 (m, 9H, Ar-H)	-	81.58 81.48		3.52 3.42
42	82	250-252	1620, 1570	0.85 (s, 12H, $>_{\text{CH}_3}^{\text{CH}_3}$), 1.75 (s, = C-CH ₂ -),				
10-(methylphenyl) C ₂₄ H ₂₉ NO ₂	02	lit [9] 249-250	1020, 1010	2.25 (s, 3H, Ar-CH ₃), 2.5 (s, 4H, -CO-CH ₂ -), 3.25 (s, 2H, =C-CH ₂ -C=), 7.1-7.55 (AB q, 4H, Ar-H)	_	_	_	-
ь	83	249-251	1630, 1580	0.9 (s, 12H, $>_{\text{CH}_3}^{\text{CH}_3}$), 1.8 (s, 4H, = C-CH ₂ -),		71.05	6 02	264
10-(4-chlorophenyl) C ₂₃ H ₂₆ NO ₂ Cl	05	247-231	1030, 1380	2.3 (s, 4H, -CO-CH ₂ -), 3.3 (s, 2H, =C-CH ₂ -C=), 7.3-7.7 (AB q, 4H, Ar-H)	_	71.95 71.84		3.64 3.54
23-26-020-								
c	84	218-220	1620, 1570	0.95 (s, 12H, C_{CH_3}), 1.90 (s, 4H, = C-CH ₂ -),	-	75.95	7.70	3.69
10-(4-methoxy- phenyl) C ₂₄ H ₂₉ NO ₃				2.3 (s, 4H, -CO-CH ₂), 3.3 (s, 2H, =C-CH ₂ -C=), 3.95 (s, 3HOCH ₃), 7.05-7.3 (AB q, 4H, Ar-H)		75.81	7.56	3.71
d	76	246-248	1630, 1580	$0.95 \text{ (s, 12H, } > \overset{\text{CH}_3}{\sim} (1, 1.6-2.2 (q, 4H, 1.6$	_	75.95	6.82	3 64
10-(2-chlorophenyl) C ₂₃ H ₂₆ NO ₂ Cl	, 0	w 10	1000, 1000	=C-CH ₂ -), (J _{gem} = 20 Hz), 2.35 (s, 4H, -CO-CH ₂), 3.3 (bs, 2H, =C-CH ₂ -C=), 7.4-8.0 (m, 4H, Ar-H)	_	75.85		3.54
e	78	232-234	1620, 1580	0.95 (s, 12H, $>$ CH ₃ CH ₃), 1.4-1.9 (q, 4H,	_	79.30	8 N4	3.85
10-(2-methylphenyl) C ₂₄ H ₂₉ NO ₂	. •		1020, 1000	=C-CH ₂ -), (J _{gem} = 18 Hz), 2.25 (s, 7H, CO-CH ₂ -, Ar-CH ₃), 3.25 (bs, 2H, =C-CH ₂ -C=), 7.2-7.6 (m, 4H, Ar-H)		79.12		3.75

Table 2

Compound	U	v	Fluorescence	Laser		
No.	$\lambda_{ ext{max}}$ nm	$\epsilon_{ ext{max}}$	λ _{max} nm	λ _{max} nm [b]	Yield [a] %	
2a	381	6185	435	477	50	
b	378	7339	435	480	50	
c	378	8679	434	478	50	
d	379	8627	435	475	50	
e	379	8157	435	478	5	
f	382	8400	435	480	5	
k	386	9000	446	490	10	
3a	370	8579	441	490	55	
ь	368	8439	438	492	50	
d	368	7738	443	498	20	
e	362	7709	441	492	20	
4a	390	8852	455	496	15	
b	385	8293	445	494	15	
c	390	8340	456	494	15	
d	386	8261	450	494	15	
e	392	8424	454	490	15	

[a] Relative laser efficiency with respect to Coumarin 102 ASE: 480 nm (methanol). [b] Concentration 15 mmoles/1; 2a-e in acetonitrile, 2f in dichloromethane, all others in methanol.

2,2'-Methylenebis(cyclohexane-1,3-dione) 1a was prepared from cyclohexane-1,3-dione [10] and formalin by stirring at 40-45° for 10 minutes in aqueous methanol, yield 96%, mp 130-132° lit [11] 132°. Other tetraketones 1b-g were prepared likewise from the respective diketone and aldehyde 1b, 93%, 148-150°; 1c, 95%, 94-96°; 1d, 90%, 205-207°, lit [11] 208°; 1e, 96%, 238-240°; 1f, 95%, 118-120°; 1g, 97%, 186-188°, lit [11] 187-188°.

Method A.

10-Aryl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinediones.

A mixture of 2,2'-methylenebis(cyclohexane-1,3-dione) 1 (1.18 g, 5 mmoles) and p-toludine (0.535 gm, 5 mmoles) was stirred in ethanol (70 ml) with a catalytic amount of phosphorus pentoxide at room temperature for 12 hours. The reaction mixture was concentrated under vacuum and poured into crushed ice; the 10-(4-methylphenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione 2a separated as a pale yellow solid and was filtered, dried and crystallised from chloroform-benzene. Other acridinediones 2b-k and 3a-e were also prepared likewise (refer to Table 1 for data). Method B.

A mixture of 2,2'-arylidenebis(cyclohexane-1,3-dione) (5 mmoles) and the respective aniline (5 mmoles) was refluxed in acetic acid (10 ml) for 1.5 hours. The reaction mixture was concentrated under vacuum and poured into crushed ice. The oily product was extracted with chloroform, dried over anhydrous magnesium sulfate and concentrated; the residue obtained was chromatographed over a column of silica gel and eluted with ethyl acetate-benzene (1:1) to isolate the respective 9-arylacridinediones 3f-h.

Method C.

10-(p-Terphenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridine-dione (2l).

A mixture of 2,2'-methylenebis(cyclohexane-1,3-dione) (1.18 g, 5 mmoles) in 10% acetic acid in ethanol (50 ml) was refluxed for

12 hours. The reaction mixture was concentrated, poured into crushed ice, the oily product obtained was extracted with chloroform, dried over anhydrous magnesium sulfate and concentrated. The residue obtained was chromatographed over a column of silica gel and eluted with ethyl acetate-benzene (1:1) to afford 21.

A mixture of the methylenebisdimedone (1 g) (5 mmoles) and the aromatic amine (5 mmoles) was refluxed in ethanol (50 ml) in the presence of a catalytic amount of phosphorus pentoxide for 6 hours. The reaction mixture was concentrated, cooled and poured into crushed ice. The bright yellow solid obtained was filtered and crystallised from chloroform to isolate the product 4a-e.

Laser Studies.

Method D.

The absorption and corrected fluorescence spectra were recorded with solutions of 10 µM concentrations. The lasing performance of the dyes was investigated by taking the solutions in a quartz cuvette and transversly exciting it by a Nitrogen laser (peak power 100 KW, wave length 337.1 nm; pulse duration 20 ns and pulse repetition 1 pps) and Nd-YAG laser (peak power 5 MW, wave length 355 nm; pulse duration 6 ns, pulse repetition 1 pps). The dye cuvette was kept tilted to avoid feed back from its walls. The wave length maximum was measured by using a constant deviation spectrometer with Hg as a reference in Nitrogen laser and monochromater-photodiode-oscilloscope combination in Nd-YAG laser. The laser characteristics i.e. efficiency, tunable range etc. were compared with a well known laser dye coumarin 102 under similar conditions. The laser data is furnished (along with uv and fluorescence data) in Table 2 for the compounds which showed measurable laser intensity.

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