Heteroatom Chemistry
Volume 7, Number 1, 1996

Synthesis of Acridinedione Derivatives as Laser Dyes

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Received 20 February 1995; revised 20 May 1995

ABSTRACT

Synthesis of 9-alkyl, 10-alkyl, 9,10-dialkyl, and 10-aryl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)acridinedione (**2a–r**) *are described as a new class of laser dyes. Reactions of diamines with methylene bis(cyclohexane-1,3-dione) yielded the respective bisacridinediones* (**3a–e**). *These dyes lase around 478–494 nm and are compared with the standard dye coumarin-102.*

INTRODUCTION

Laser is an acronym for light amplification by stimulated emission of radiation. In recent years, the research in the laser field has drawn considerable attention due to its wide range of applicability. In addition to the primary sources of laser activity, such as solid-state lasers (Nd-YAG) and molecular gas lasers (N_2, CO_2), organic compounds have been used as active media and are called dye lasers [1]. The first demonstration of a dye laser was reported in 1966 by Sorokin and Lankard [2].

In 1984, Maeda listed about 600 compounds as laser dyes [3]. These dye lasers are broadly classified as cyanine or polymethine dyes, xanthene dyes (Rhodamine 6G), linear and condensed polybenzoid compounds, and heterocyclic compounds. In the heterocyclic compounds, coumarin-102 and carbostyril-124 are common examples. So far, only very few acridine derivatives have been reported as laser dyes, such as acridine yellow [4], 9-aminoacridine hydrochloride [5], 9-(10H)acridone [6], acriflavine [7,8], *N*-methylacridinium perchlorate [9], lucigenin [10], and carbazine [11].

RESULTS AND DISCUSSION

In continuation of our preliminary report [12] and studies on a search for a new class of dye lasers [13,14], we herein report the synthesis of acridinediones and their laser activity. Condensation of cyclohexane-1,3-diones with aldehydes furnished the tetraketone (**1**), which, on reaction with ammonia or amines under different conditions, afforded the acridinediones. The reactions in general were carried out with a catalytic amount of P_2O_5 in methanol at room temperature. Acetic acid, with or without methanol, under reflux was sometimes necessary for the condensation and especially for the reactions with diamines. The 10-unsubstituted acridinediones were prepared by reaction of the tetraketones with aqueous ammonia or ammonium acetate in acetic

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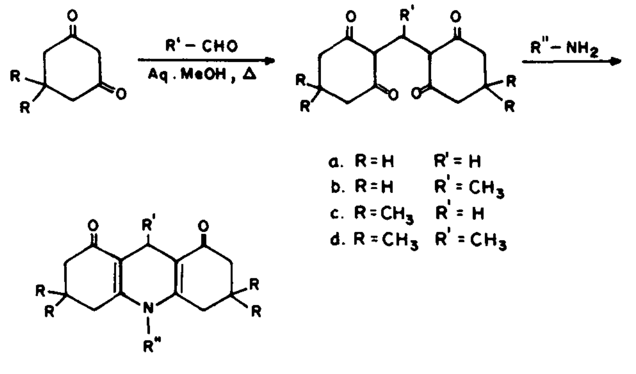
1042-7163/96/010017-06

acid. The amines used in the present study include methylamine, glycine, anthranilic acid, 2-aminopyrene, and 4-aminobiphenyl. In the case of diamines, 1,2-phenylenediamine gave only the monoacridine derivative (**2k**); 1,4-phenylenediamine, benzidine, 4,4″-diamino-*p*-terphenyl, 4,4′-diaminodiphenylmethane, and ethylenediamine gave the bis-acridinediones (**3a–e**).

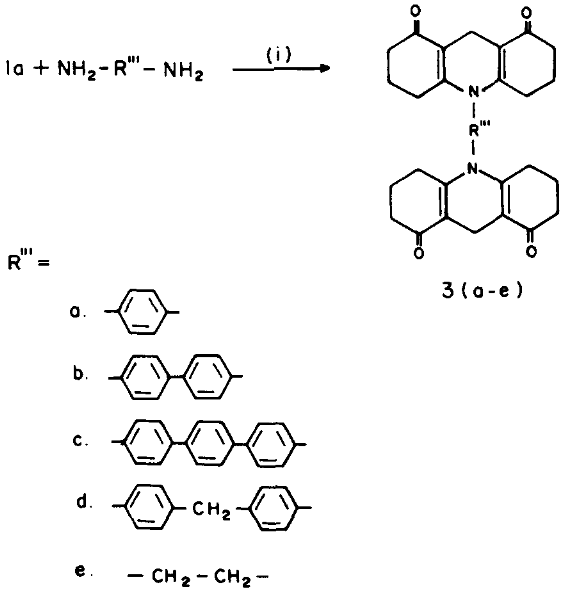
The ^{1}H NMR spectra of all of the acridinediones in general showed characteristic signals (Table 1). For compound **2d**, the C3 and C6 methylene protons were seen in the range δ 2.0–2.2 as a multiplet; the C4 and C5 methylene protons appeared at δ 2.3–2.5 as a multiplet; the C2 and C7 methylene protons were seen at δ 2.55–2.75. The signals of C4 and C5 methylene protons invariably merged with the C3 and C6 methylene signals (e.g., **2a**, **2e**, **2f**, **2g**, **2h**, **2j**, **2k**) or with the C2 and C7 methylene signals (e.g., **2b**, **2c**). The C9 methylene protons appeared as a singlet in general around δ 3.1; however, a geminal coupling of 20 Hz in **2i** and **2l** was seen. In the case of **2i**, the pyrenyl group makes the two protons of the C9 methylene nonequivalent; a similar effect is observed caused by the formamido group in compound **2l**. This nonequivalence of the C9 methylene protons is in line with the earlier observation wherein the 10-(2-chloro-6-methylphenyl)- and 10-(2,4-dimethyl-6-bromophenyl)acridinediones showed the C9 methylene as a quartet with a geminal coupling of 20 Hz [14]. The previously mentioned nonequivalence of the C9 methylene protons caused by the 10-aryl group can be rationalized based on X-ray crystallographic studies on some of the acridinediones [15,16]. The IR spectra showed the characteristic peak between 1610–1650 cm^{-1} for the carbonyl group. The mass spectra of the acridinediones in general showed the molecular ion peak as the base peak.



2 (a-r)

Compound	*R*	*R′*	*R″*
2a	H	H	H
b	H	H	CH_3
c	H	CH_3	H
d	H	CH_3	CH_3
e	H	H	CH_2COOH
f	H	H	3-$C_6H_4NO_2$
g	H	H	2-C_6H_4COOH
h	H	H	2-$C_6H_4COOCH_3$
i	H	H	2-Pyrenyl
j	H	H	4-biphenylyl
k	H	H	2-C_6H_4-NH_2
l	H	H	2-C_6H_4NHCHO
m	CH_3	H	H
n	CH_3	H	CH_3
o	CH_3	CH_3	H
p	CH_3	CH_3	CH_3
q	CH_3	H	n-butyl
r	CH_3	H	CH_2-COOH

Table 2 gives the absorption, emission, and lasing characteristics of the dyes that have high lasing efficiencies using methanol as solvent. A close look at the structures of the compounds reveals that substitution on the nitrogen and the 9-position have an influence on the lasing yields. As compared with compounds of the same class reported earlier [13], which have aryl substituents on the nitrogen, these compounds, which are unsubstituted or methyl substituted, have lasing efficiencies comparable to that of coumarin-102, whereas with aryl substituents, lasing efficiency was only 50%. However, the compounds that are unsubstituted on the nitrogen and the 9-position have lasing yields higher than that of coumarin-102; a substitution on the nitrogen or on



3 (a-e)

a. $MeOH/P_2O_5$/r.t.stirring (2f-h,k)
b. MeOH/AcOH/Δ (2b,d)
c. AcOH/Δ (2e,i,j,q,r,3a–e)
d. aq. ammonia/Δ (2a)
e. NH_4OAc in AcOH (2c)

TABLE 1 Physical Data of Acridinediones **2** and **3**

Compound	*Yield (%)*	*m.p. (°C)*	*IR (cm^{-1})*	*^{1}H-NMR ($CDCl_3$-DMSO-d_6) (δ)*	*MS*	*Analysis Calculated/Found*		
						C	*H*	*N*
2a $C_{13}H_{15}NO_2$	85	>300 lit. [9] 270	3280 1625 1590	2.25–2.45 (m,8H) 2.55–2.65 (m,8H) 3.0 (s,2H) 7.9 (s,1H)				
b $C_{14}H_{17}NO_2$	82	202–204	1615 1560	1.80–2.2 (m,4H) 2.3–2.6 (m,8H) 3.10 (s,2H) 3.2 (s,3H)		72.70 72.56	7.40 7.26	6.05 6.20
c $C_{14}H_{17}NO_2$	88	294–296	3290 1620 1595	0.90 (d,3H) 1.95–2.15 (m,4H) 2.25–2.60 (m,8H) 3.85–4.05 (q,1H) 8.95 (s,1H)	231 (M^+)	72.70 72.42	7.40 7.58	6.05 6.11
d $C_{15}H_{19}NO_2$	89	296–298	1620 1560	0.80 (d,3H) 2.02–2.2 (m,4H) 2.3–2.5 (m,4H) 2.55–2.75 (m,4H) 3.30 (s,3H) 3.95–4.15 (q,1H)		73.44 73.52	7.80 7.79	5.70 5.77
e $C_{15}H_{17}NO_4$	80	182–184	1685 1610 1375	1.9–2.2 (m,8H) 2.3–2.5 (m,4H) 3.1 (s,2H) 3.2 (s,2H)		65.44 65.18	6.22 6.12	5.08 4.99
f $C_{19}H_{18}N_2O_4$	82	226–228	1625 1580 1520 1340	1.9–2.0 (m,8H) 2.3–2.4 (m,4H) 3.2 (s,2H) 7.4–8.3 (m,4H)	338 (M^+)	67.44 67.13	5.36 5.16	8.27 8.06
g $C_{20}H_{19}NO_4$	79	262–264	1710 1640 1610 1600	1.90–2.10 (m,8H) 2.3–2.45 (m,4H) 3.15 (bs,2H) 7.5–8.2 (m,4H)	337 (M^+)	71.20 71.11	5.67 5.47	4.15 4.01
h $C_{21}H_{21}NO_4$	78	142–144	1710 1630 1600 1580	1.80–2.0 (m,8H) 2.20–2.4 (m,4H) 3.10 (s,2H) 3.9 (s,3H) 7.5–8.2 (m,4H)	351 (M^+)	71.77 71.57	6.02 5.96	3.98 3.69
i[a] $C_{29}H_{23}NO_2$	79	265–268	1630 1590 1580	1.7–1.8 (m,6H) 1.96–2.04 (m,2H) 2.39 (t,4H) 3.38–3.48 (2H,dd; J_{gem} = 20 Hz) 7.9–8.34 (m,9H)	417 (M^+)	83.42 83.22	5.55 5.35	3.35 3.29
j $C_{25}H_{23}NO_2$	77	238–240	1625 1595 1575	1.80–2.1 (m,8H) 2.25–2.45 (m,4H) 3.25 (s,2H) 7.30–785 (m,9H)	369 (M^+)	81.27 81.01	6.27 6.11	3.79 3.56
k $C_{19}H_{20}N_2O_2$	84	258–260	3380 3300 1640 1600 1500	1.90–2.20 (m,8H) 2.35–2.50 (m,4H) 3.20 (s,2H) 3.90 (bs,2H) 6.90–7.40 (m,4H)		74.00 73.92	6.53 6.36	9.08 8.91
l[a] $C_{20}H_{20}N_2O_3$	72	160–162	3280 1695 1630 1610 1590	1.88–1.98 (m,6H) 2.02–2.08 (m,sH) 2.40 (t,4H) 3.16–3.32 (dd,2H, J_{gem} = 20 Hz) 7.2–7.5 (m,4H) 8.55 (d,1H) 8.65 (s,1H)	336 (M^+)	71.41 71.26	5.99 5.86	8.32 8.16

TABLE 1 Continued

Compound	Yield (%)	m.p. (°C)	IR (cm^{-1})	^{1}H-NMR ($CDCl_3$–DMSO-d_6) (δ)	MS	Analysis Calculated/Found C	H	N
m	88	317–319 lit. [21] 319–321						
n	81	226–228 lit. [22]						
o	92	256–258 lit. [23] 259–261						
p	86	206–208 lit. [22]						
q $C_{21}H_{31}NO_2$	82	164–166	1620 1570	0.9–1.6 (m,19H) 2.25 (s,4H) 2.40 (s,4H) 3.10 (s,2H) 3.50 (t,2H)		76.55 76.29	9.48 9.28	4.25 4.11
r $C_{19}H_{25}NO_4$	85	174–176	1690 1610 1380	1.10 (s,12H) 2.25 (s,4H) 2.40 (s,4H) 3.10 (s,2H) 3.20 (s,2H)		68.85 68.59	7.60 7.38	4.22 4.16
3a^a $C_{32}H_{32}N_2O_4$	78	>300	1640 1580	1.90 (quin,8H) 2.04 (t,8H) 2.34 (t,8H) 3.14 (s,4H) 7.82 (s,4H)	508 (M$^+$)	75.56 75.36	6.34 6.18	5.50 5.39
b^a $C_{38}H_{38}N_2O_4$	76	>300	1635 1585	1.90 (m,8H) 2.04 (m,8H) 2.40 (m,8H) 3.26 (s,4H) 7.4 & 7.8 (ABq,8H, 8Hz)		78.05 78.15	6.20 6.09	4.79 4.59
c^a $C_{44}H_{40}N_2O_4$	72	>300	1640 1600 1580	1.80 (quin,8H) 2.04 (t,8H) 2.38 (t,8H) 3.26 (s,4H) 7.28 & 7.65 (ABq,8H) 7.80 (s,4H)		79.97 79.69	6.10 6.10	4.23 4.11
d^a $C_{39}H_{38}N_2O_4$	81	294–296	1640 1575	1.85 (quin,8H) 2.0 (t,8H) 2.35 (t,8H) 3.25 (s,4H) 4.15 (s,2H) 7.20–7.33 (ABq,8H,8Hz)	596 (M$^+$)	78.23 78.12	6.39 6.18	4.67 4.46
e^a $C_{28}H_{32}N_2O_4$	79	>300	1640 1580	1.95–2.25 (m,8H) 2.25–2.35 (m,8H) 2.45–2.55 (m,8H) 3.10 (s,4H) 3.85 (s,4H)	245 (M$^+$ −215)	73.01 72.91	7.00 6.91	6.08 6.01

[a] 500 MHz ^{1}H NMR for **2i, 2l, 3a–e**.

the 9-position decreases the lasing yield slightly. The tuning range for the dyes lies between 470 and 510 for all the dyes chosen.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 258 spectrophotometer on KBr discs. The ^{1}H NMR spectra were recorded on Varian-EM 390 (90 MHz) and 500 MHz spectrometers. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS instrument. Laser data were obtained using a Quanta-Ray DCR 2 Nd-YAG laser. Chromatographic purifications were performed on silica gel (100–200 mesh). The absorption spectra

TABLE 2 Laser Data of Acridinediones **2**

Compound No.	Absorption	Extinction log ε coefft. (M^{-1} cm^{-1})	Emission$_{max}$	Laser			
				λ_{max} (nm)	Yield[a] (%)	Range (nm)	Conc.[b] mmol/lit.
2a	386	3.96	445	478	113	475–488	4
2b	396	3.73	460	480	88	465–514	15
2c	372	3.97	441	480	100	470–490	10
2d	380	3.97	457	483	108	455–514	10
2e	396	3.94	468	485	76	472–506	10
2m	388	3.62	446	482	116	474–500	10
2n	400	3.92	468	490	84	470–510	10
2o	375	3.82	442	485	98	476–492	10
2p	380	3.95	461	491	109	480–510	10
2r	398	3.95	468	494	83	473–512	10

[a] Relative efficiency with respect to coumarin-102, ASE 470 nm (methanol).
[b] In methanol (concentration of standard dye coumarin-102 is 10 mmol/lit.)

were recorded on a Hitachi-320 spectrophotometer, and fluorescence spectra were recorded on an LS5B Perkin-Elmer fluorescence spectrometer. For the lasing studies, the concentrations were chosen at which the lasing yield was maximum. The lasing action was measured by exciting the dye solutions using the third-harmonic output from an Nd-YAG laser (peak power 50 mJ, 355 nm; pulse duration 6 ns, pulse rep. rate 10 Hz). The dye cuvette was kept tilted in order to avoid feedback from the walls. The output from the dye was focused on an integrating photodiode whose output was seen as a pulse in an HP Oscilloscope that was interfaced to a computer in order to obtain the integrated area under the curve. The ratio of the integrated area for the dye and the reference, coumarin-102, gave the lasing efficiency of the dye. The amplified stimulated emission (ASE) spectrum was obtained by introducing a monochromator between the dye laser cuvette and the integrating photodiode.

2,2′-Methylenebis(cyclohexane-1,3-dione) **1a** was prepared from cyclohexane-1,3-dione and formalin by stirring at 40–45°C for 10 minutes in aq. methanol [17]; yield 96%; m.p. 130–132°C; lit. 132°C [18]. Other tetraketones **1b–d** were prepared likewise from the corresponding diketone and aldehyde; **1b**, 93%; m.p. 152–154°C; lit. 155°C [18]; **1c**, 97%; m.p. 186–188°C; lit. 191°C [19]; **1d**, 95%; m.p. 126–128°C; lit. 141–142°C [20].

Preparation of Acridinediones

Method a. 10-(3-Nitrophenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H)-acridinedione (**2f**). A mixture of 2,2′-methylenebis(cyclohexane-1,3-dione) **1a** (1.18 g, 5 mmol) and 3-nitroaniline (0.69 g, 5 mmol) was stirred in methanol at room temperature with a catalytic amount of P_2O_5 for 8 hours. The solvent was removed under vacuum and the residue poured into crushed ice. The solid obtained was filtered off, dried, and crystallized from chloroform-methanol to yield **2f**.

Method b. 10-Methyl-3,4,6,7,9,10-hexahydro-1,8-(2H,5H)-acridinedione (**2b**). A mixture of 2,2′-methylenebis(cyclohexane-1,3-dione) (**1a**) (1.18 g, 5 mmol) and a 40% aqueous solution of methylamine (0.4 mL) was refluxed in 50% acetic acid-methanol (50 mL) for 12 hours. The reaction mixture was concentrated and poured into crushed ice. The solid obtained was filtered off, dried, and crystallized from chloroform-methanol to yield **2b**.

Method c. 1,4-Bis(3,4,6,7,9,10-hexahydro-1,8 (2H,5H)-acridinedione-10-yl)-benzene (**3a**). A mixture of 2,2′-methylenebis(cyclohexane-1,3-dione) (**1a**) (5 mmol) and 1,4-phenylenediamine (2.5 mmol) was refluxed in acetic acid (10 mL) for 2 hours. The reaction mixture was concentrated under reduced pressure and poured into crushed ice. The solid obtained was filtered off, dried, and chromatographed over a column of silica gel and eluted with chloroform to get **3a**.

Method d. 3,4,6,7,9,10-Hexahydro-1,8(2H,5H)-acridinedione (**2a**). The tetraketone **1a** (1.18 g, 5 mmol) was heated on a steam bath, with aq. ammonia (10 mL) for 2 hours. The solid obtained was filtered off, dried, and crystallized from chloroform-methanol to get **2a**.

Method e. 9-Methyl-3,4,6,7,9,10-hexahydro-1,8 (2H,5H)acridinedione (**2c**). The tetraketone **1b** (1.25 g, 5 mmol) was refluxed in acetic acid (15 mL) with ammonium acetate (0.46 g, 6 mmol) for 2 hours. The excess acetic acid was removed and the residue cooled and poured into crushed ice; the solid was filtered off, dried, and crystallized from chloroform-methanol to yield **2c**.

10-(2-Formamidophenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H)acridinedione(**2l**). The 10-(2-aminophenyl)acridinedione (**2k**) (1.54 g, 5 mmol) was refluxed in formic acid (5 mL) for 3 hours, cooled, and poured into crushed ice; the solid obtained was filtered off, dried, and crystallized from DMF-water to get **2l**.

The syntheses of 2 m-p are described elsewhere [21,22,23].

ACKNOWLEDGMENT

We wish to thank the Department of Science and Technology and the University grants commission (New Delhi) Special assistance program for financial assistance, Professor J. H. Boyer, University of New Orleans and Professor J. Kagan, University of Illinois at Chicago for mass spectra, and IIT, Madras for spectral and analytical data. One of the authors (N.S) is thankful to CSIR for a fellowship. The Department of Inorganic Chemistry is thankful to the UGC-COSIST program for financial support for the fluorimeter and laser facilities.

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