Synthesis and laser properties of 9-alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione derivatives

P. Murugan,[a] P. Shanmugasundaram,[a] V. T. Ramakrishnan,*,[a] B. Venkatachalapathy,[b] N. Srividya,[b] P. Ramamurthy,[b] K. Gunasekaran[c] and D. Velmurugan[c]

[a] *Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai – 600 025, India*
[b] *Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai – 600 025, India*
[c] *Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai – 600 025, India*

9-Alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione derivatives 2, 3, 4 have been prepared and their absorption, emission and laser properties have been evaluated. A crystal structure determination for the compound 2d has also been performed.

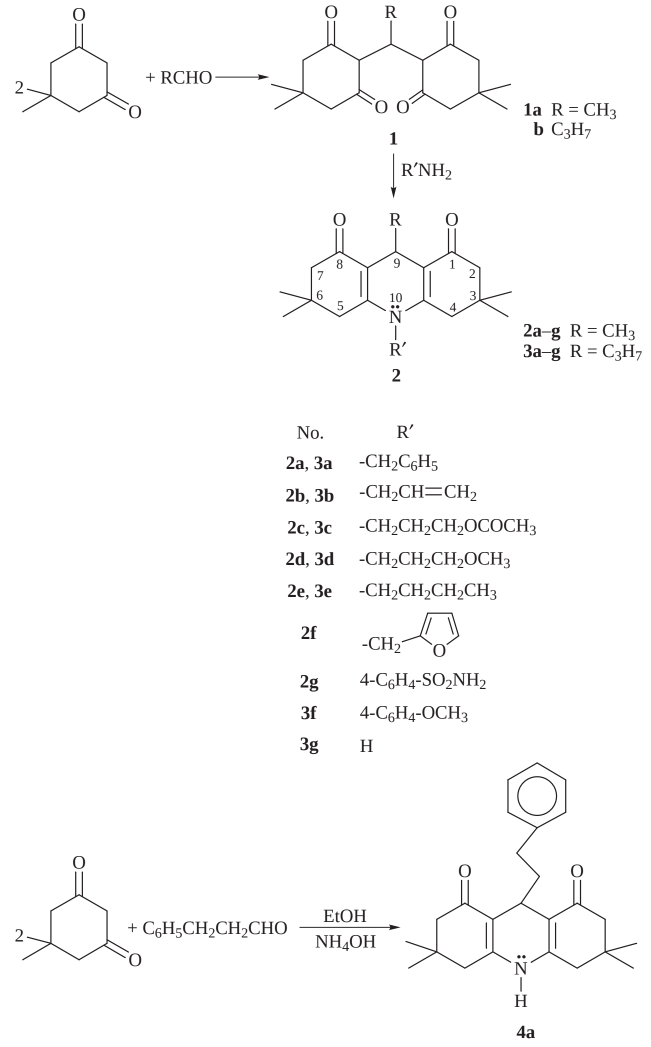
Introduction

Many organic compounds have been found to possess laser activity,[1] in the region 310–1100 nm. These dye lasers have been classified as polymethine dyes, xanthene dyes, heterocyclic compounds, *etc.* Rhodamine in the xanthene class and coumarin in the heterocyclic group have become well known for their laser properties. Only a few examples in the acridine ring system are known to possess laser activity.[1] We have observed that the 1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione ring system shows laser activity at about 480 nm.[2] Since then various acridinediones with alkyl/aryl substituents at the 9- and 10-positions have been synthesised.[3,4] The acridinedione ring also shows electrochemical properties[5] and interacts with DNA.[6] Based on the above observations, we have synthesised various substituted acridinediones and studied their spectral properties.

Results and discussion

The method of synthesis of the acridinediones was essentially the same as reported previously.[4] 5,5-Dimethylcyclohexane-1,3-dione was condensed with acetaldehyde/butyraldehyde to yield the respective tetraketone which was treated with various amines in refluxing acetic acid to give the corresponding acridinedione. Reaction with aminoethanol gave the respective acetylated compounds (**2c**, **3c**) (Scheme 1). The products were purified by column chromatography followed by crystallization from MeOH–$CHCl_3$. The acridinediones were characterized by IR, ^1H NMR, ^{13}C NMR and mass spectroscopy, elemental analysis and X-ray crystallography. The IR spectrum shows a characteristic peak in the 1650 cm^{-1} region. The ^1H NMR data were consistent with the respective structures. A characteristic coupling pattern in the ^1H NMR spectra was observed in certain cases (Table 1).

The C^2H_2 (and C^7H_2) is observed as a singlet at δ 2.2 for the acridines with no substituent on C^9.[5] A CH_3 group on C^9, has little effect on C^2H_2 thereby also giving a singlet for **2a**,**b**,**e**–**g**. However, depending upon the substituent at the 10-position, geminal coupling is observed for C^2H_2 ($J = 16.7$ Hz), as in compound **2c**. In compounds with 9-propyl derivatives, C^2H_2 exhibits geminal coupling as seen in **3b**–**e** in the range δ 2.2–2.5 (Fig. 1). The alkyl substituent on the nitrogen apparently causes the C^2-methylene hydrogens to be magnetically inequivalent while the effect of benzyl (**3a**) or *p*-anisyl (**3f**) is much less.



Scheme 1

In the case of C^4H_2 (and C^5H_2) all the compounds (**2a**–**g**; **3a**–**g**) show geminal coupling, due to the presence of a CH_3 or *n*-C_3H_7 at C^9 and a substituent at the 10-position. In the case

Table 1 ^{1}H NMR data for compounds **2a**–**g**, **3a**–**g** and **4a** (*J* values are given in Hz)

Compound	$\mathrm{C^2H_2}$ and $\mathrm{C^7H_2}$ protons	$\mathrm{C^4H_2}$ and $\mathrm{C^5H_2}$ protons	Other protons
2a	2.23 (s)	2.20–2.41 (ABq, *J* 16.5)	0.84 (d, $\mathrm{C}H_3\mathrm{–CH}$), 0.94–0.98 (2 × s, *gem*-dimethyl), 4.1 (q, $\mathrm{C}H\mathrm{–CH_3}$), 4.82 (s, $\mathrm{Ar–C}H_2$), 7.15–7.41 (m, ArH)
2b	2.22 (s)	2.27–2.41 (ABq, *J* 16.2)	0.91 (d, $\mathrm{C}H_3\mathrm{–CH}$), 1.03 (s, *gem*-dimethyl), 4.06 (q, $\mathrm{C}H\mathrm{–CH_3}$), 4.19 (d, $\mathrm{N–CH_2}$), 5.16 and 5.3 (2 × d, $\mathrm{CH{=}C}H_2$), 5.95 (m, $\mathrm{C}H\mathrm{{=}CH_2}$)
2c	2.25, 2.27 (ABq)	2.30, 2.54 (ABq, *J* 16.7)	0.85 (d, $\mathrm{C}H_3\mathrm{–CH}$, *J* 6.4), 1.10, 1.12 (2 × s, *gem*-dimethyl), 2.06 (s, $\mathrm{OCOCH_3}$), 3.96 (t, $\mathrm{N–C}H_2$, *J* 5.8), 4.05 (q, $\mathrm{C}H\mathrm{–CH_3}$, *J* 6.4), 4.17 (t, $\mathrm{OC}H_2$, *J* 5.8)
2d	2.23, 2.26 (ABq)	2.35, 2.51 (ABq)	0.84 (d, $\mathrm{C}H_3\mathrm{CH}$, *J* 6.3), 1.10 (s, *gem*-dimethyl), 1.9 (m, $\mathrm{N–CH_2–C}H_2$), 3.38 (s, $\mathrm{OCH_3}$), 3.5 (t, $\mathrm{N–C}H_2$), 3.62 (t, $\mathrm{OCH_2}$), 4.1 (q, $\mathrm{C}H\mathrm{–CH_3}$)
2e	2.23 (s)	2.35, 2.42 (ABq)	0.87 (d, $\mathrm{C}H_3\mathrm{–CH}$), 1.08 (s, *gem*-dimethyl), 1.5 (m, butyl-$\mathrm{CH_2}$–), 3.60 (t, $\mathrm{N–C}H_2$), 4.06 (q, $\mathrm{C}H\mathrm{–CH_3}$)
2f	2.25 (s)	2.3, 2.5 (ABq)	0.85 (d, $\mathrm{C}H_3\mathrm{–CH}$), 1.05 (s, *gem*-dimethyl), 4.05 (q, $\mathrm{C}H\mathrm{–CH_3}$), 4.75 (s, $\mathrm{N–CH_2}$) 6.2, 6.4 and 7.4 (furfuryl-H)
2g	2.23 (s)	1.7, 1.95 (ABq, *J* 15)	0.94, 0.96 (2 × s, *gem*-dimethyl), 1.06 (d, $\mathrm{C}H_3\mathrm{–CH}$), 4.1 (q, $\mathrm{C}H\mathrm{–CH_3}$), 5.0 (s, $\mathrm{NH_2}$, with $\mathrm{D_2O}$ exchange), 7.3 and 8.1 (ABq, Ar-H) Ar–H)
3a	2.2 (s)	2.25, 2.40 (ABq)	0.79 (t, $\mathrm{C}H_3\mathrm{–CH_2}$), 0.98 (s, *gem*-dimethyl), 1.1–1.2 (m, $\mathrm{C}H_2\mathrm{–CH_2}$), 4.9 (s, $\mathrm{N–CH_2}$), 7.1–7.4 (m, ArH)
3b	2.22, 2.24 (ABq)	2.3, 2.4 (ABq, *J* 16)	0.79 (t, $\mathrm{CH_3–CH_2}$, *J* 7), 1.03, 1.05 (2 × s, *gem*-dimethyl), 1.1–1.3 (m, $\mathrm{C}H_2\mathrm{–CH_2}$), 4.17 (m, $\mathrm{C^9H}$ and $\mathrm{N–CH_2}$), 5.1–5.4 (2 × d, $\mathrm{C}H_2\mathrm{{=}CH}$), 5.9 (m, $\mathrm{C}H\mathrm{{=}CH_2}$)
3c	2.2, 2.25 (ABq)	2.3, 2.55 (ABq)	0.8 (t, $\mathrm{C}H_3\mathrm{–CH_2}$), 1.08, 1.1 (2 × s, *gem*-dimethyl), 1.13–1.3 (m, $\mathrm{CH_3C}H_2\mathrm{–C}H_2$), 2.05 (s, $\mathrm{OCOCH_3}$), 3.95 (t, $\mathrm{N–CH_2}$), 4.1–4.2 (m, $\mathrm{OCH_2}$ and $\mathrm{C^9H}$)
3d	2.2, 2.55 (ABq)	2.3, 2.55 (ABq)	0.8 (t, $\mathrm{C}H_3\mathrm{–CH_2–CH_2}$), 1.1 (2 × s, *gem*-dimethyl), 1.0–1.3 (m, $\mathrm{CH_3–C}H_2\mathrm{–C}H_2$), 1.8 (m, $\mathrm{N–CH_2–C}H_2$), 3.35 (s, $\mathrm{OCH_3}$), 3.4 (t, $\mathrm{N–CH_2}$), 3.75 (t, $\mathrm{OCH_2}$), 4.1 (m-$\mathrm{C^9H}$)
3e	2.23, 2.27 (ABq)	2.3, 2.5 (ABq)	0.8 (t, $\mathrm{C}H_3\mathrm{–CH_2–CH_2}$), 1.0 (t, $\mathrm{CH_3}$ of N-butyl), 1.09, 1.1 (2 × s, *gem*-dimethyl), 1.1–1.6 (m, propyl, butyl $\mathrm{CH_2}$), 3.6 (t, $\mathrm{N–CH_2}$), 4.1 (t, $\mathrm{C^9H}$)
3f	2.23 (s)	1.7–2.1 (ABq, *J* 17.4)	0.89 (t, $\mathrm{C}H_3\mathrm{–CH_2–CH_2}$, *J* 7.0) 0.96, 0.97 (2 × s, *gem*-dimethyl), 1.25–1.50 (m, $\mathrm{CH_3–C}H_2\mathrm{–C}H_2$), 3.92 (s, $\mathrm{OCH_3}$), 4.24 (t, $\mathrm{C^9H}$, *J* 5.0), 7.0–7.1 (m, Ar-H)
3g	2.25 (s)	2.15–2.4 (ABq)	0.8 (t, $\mathrm{C}H_3\mathrm{–CH_2–CH_2}$), 1.1 (s, *gem*-dimethyl), 1.15–1.5 (m, $\mathrm{C}H_2\mathrm{–C}H_2\mathrm{–CH_3}$), 4.1 (t, $\mathrm{C^9H}$), 5.85 (NH)
4a	2.24 (s)	2.26–2.40 (ABq, *J* 17)	1.07, 1.12 (2 × s, *gem*-dimethyl), 1.7–1.8 (m, Ar $\mathrm{CH_2–C}H_2$), 2.5 (m, Ar $\mathrm{C}H_2$), 4.2 (t, $\mathrm{C^9H}$), 7.0–7.2 (m, Ar–H), 7.76 (s, N–H)

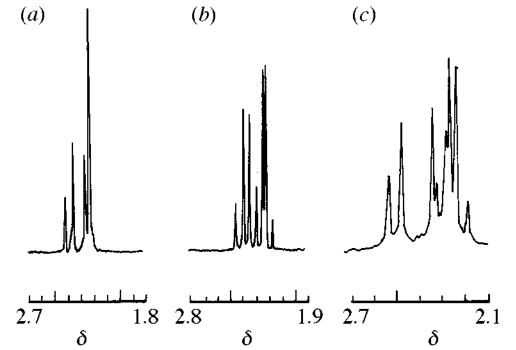


Fig. 1 $\mathrm{C^2H_2}$ and $\mathrm{C^4H_2}$ geminal coupling in the ^{1}H NMR spectra of (*a*) **2a**, (*b*) **3a** and (*c*) **3e**

of **3g** apparently the steric effect of the propyl group is sufficient to cause geminal coupling of $\mathrm{C^4H_2}$. Note that in the two compounds where $\mathrm{CH_3}$ or H replaces propyl, no geminal coupling of $\mathrm{C^4H_2}$ was observed.[4] The $\mathrm{C^4H_2}$ is apparently shielded by the directly attached aryl ring on the nitrogen in compounds **2g** and **3f**.

Geminal coupling ($J = 20$ Hz) of $\mathrm{C^9H_2}$ was observed at δ 2.8–3.4 in compounds where the *N*-aryl group had two different *ortho*-substituents (2-Cl-6-$\mathrm{CH_3}$, 2-Br-6-$\mathrm{CH_3}$), one *ortho*-substituent such as OH, OAC, NH–$\mathrm{COCH_2Cl}$, NHCHO, or where the aryl itself was 2-pyrenyl. In the case of 10-(2-methylphenyl)acridinedione, $\mathrm{C^9H_2}$ is seen as a singlet whereas the corresponding dimedone (5,5-dimethylcyclohexane-1,3-dione) compound shows geminal coupling due to the steric effect caused by the *gem*-dimethyl group in both the rings.

Absorption and emission spectral data are given in Table 2, methanol was used as the solvent for all the measurements. The absorption maxima are characteristic of the class of dyes and are in close agreement with the other dyes of the same class previously reported.[4] The earlier studies on the laser action of the dyes have concentrated on acridinediones with varying substituents on the 9-position. The absorption, emission and

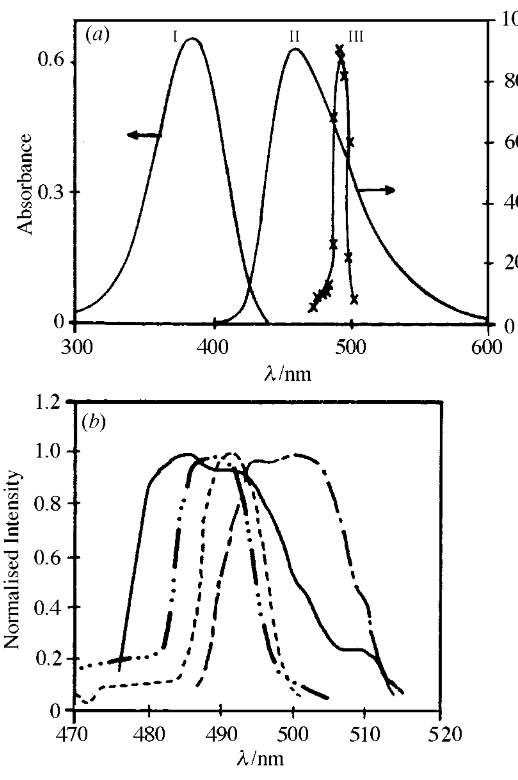


Fig. 2 (*a*) Absorption (I), emission (II) and ASE (III) spectra of **2a** in methanol. (*b*) ASE spectra of **2a** (—···), **2b** (-----), **2c** (——) and **3d** (— –) in methanol.

Table 2 Absorption, fluorescence and lasing data for the dyes in methanol

Compound	λ_{max}/nm (absorption)	log (ε/M^{-1} cm^{-1})	λ_{max}/nm (emission)	φ_f	ASE yield (%)	ASE max/nm
2a	382	3.9265	461	0.776	70	490
2b	385	3.9463	454	0.898	137	490
2c	373	3.7795	456	0.669	98	488
2d	381	3.9272	463	0.655	100	494
2e	382	3.8918	463	0.680	114	498
2f	374	3.8834	456	0.699	116	490
2g	376	3.9318	448	—	*a*	—
3a	379	3.8934	456	0.782	61	494
3b	380	3.8970	462	0.894	140	490
3c	371	3.8783	459	0.634	95	496
3d	380	3.8101	464	0.721	98	500
3e	380	3.8814	463	0.682	117	494
3f	376	3.9216	454	—	*a*	—
3g	377	3.9364	453	0.926	135	484
4a	376	3.9037	456	0.897	101	488

[a] Not lasing.

Table 3 Torsion angles (°) about the two outer rings of the compound **2d**

C1A–C1–C2–C3	46.3(6)
C2–C1–C1A–C4A	−21.8(7)
C1–C1A–C4A–C4	−2.2(8)
C1–C2–C3–C4	−48.9(6)
C2–C3–C4–C4A	28.5(7)
C3–C4–C4A–C1A	−1.8(8)
C5A–C5–C6–C7	−30.9(7)
C6–C5–C5A–C8A	2.9(8)
C5–C5A—C8A–C8	−3.1(8)
C5—C6–C7–C8	56.6(6)
C6–C7–C8–C8A	−53.5(6)
C7–C8–C8A–C5A	29.8(7)

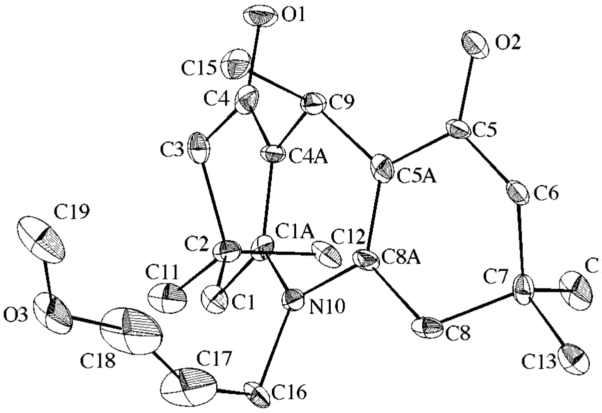


Fig. 3 ORTEP diagram of molecule **2d** with the 50% probability displacement ellipsoid

amplified spontaneous emission (ASE) spectra for compound **2a** are given in Fig. 2(*a*) and ASE spectra for compounds **2a**–**c** and **3d** are given in Fig. 2(*b*).

The compounds chosen for this study have either methyl or propyl substituents at the 9-position and varying substituents on the nitrogen centre. Previous studies have shown that a compound with no substitution on either the nitrogen or at the 9-position has the highest fluorescence quantum yield as well as the greatest lasing efficiency, while compounds with methyl substitution on the nitrogen and at the 9-position have slightly lower yields. Table 2 shows that the N–H, 9-propyl substituted compound **3g** has the highest fluorescence quantum yield of 0.93, and the N–H, 9-phenylethyl substituted compound **4a** has a quantum yield of 0.90. The lasing efficiency with respect to coumarin 102 is also greater, 135 and 101%, respectively. A benzyl substituent on the nitrogen decreased both the fluorescence quantum yield and the lasing efficiency (**2a** and **3a**). This observation is consistent with the previous reports[4] that aryl substitution decreases the fluorescence yield due to a large deactivation and shows very poor or no lasing at all. Allyl and butyl substituted compounds show lasing efficiencies comparable to or higher than that of coumarin 102. The *N*-allyl substituted compounds (**2b** and **3b**) have high fluorescence quantum yields and lasing efficiencies of 137 and 140% respectively. This shows that the presence of an allyl group, containing a $CH{=}CH_2$ moiety, aids the stimulated emission. The tuning range of the dyes lies between 470 and 510 nm with a maximum at around 490 nm. The lasing efficiencies and wavelengths are given in Table 2.

From crystallographic analysis of compound **2d** (see Fig. 3), the acridine moiety is found, from least square plane calculations, to be folded about the line passing through atoms C9 and N10 and the dihedral angle between the two halves (C9, N10, C1A, C1, C2, C3, C4, C4A and C9, N10, C5A, C5, C6, C7, C8, C8A) is 43°, this being higher than the value found for an earlier example.[7]

The ring puckering amplitudes of $Q2 = 0.329(5)$, $Q3 = 0.067(6)$ and $QT = 0.336(5)$ Å prove that the central ring is in boat form. The two outer rings are in half-chair conformations as can be seen from the torsion angles (Table 3). The two keto groups differ in bond lengths. The bond lengths in the sequence N10–C1A–C4A–C4–O1 show a high degree of delocalisation of electrons whilst much less delocalisation is present in the sequence N10–C8A–C5A–C5–O2 (Table 4). The inner angle N10–C1A–C4A [117.3(4)°] differs significantly from that of N10–C8A–C5A [123.6(5)°].

Compound **2d** is unsymmetric. The methyl group at C9 is in an equatorial position [C1A–C4A–C9–C15 = 95.5(7)° and C8A–C5A–C9–C15 = −92.2(7)°]. The geometry about the substituents is normal. The atoms O3 and C18 have high thermal vibration as they are in the flexible end group.

In addition to the van der Waals interactions, two intermolecular C–H···O hydrogen bonds [C8–H8A = 0.97(1) Å, C8···O2 $(x - \frac{1}{2}, -y + 1, z) = 3.44(1)$ Å, C8–H8A···O2 = 158.9(6)°; C1–H1A = 0.97(1) Å, C1···O1 $(x - \frac{1}{2}, -y + 1, z) = 3.46(1)$ Å, C1–H1A···O1 = 152.6(4)°] stabilize the molecules in the crystalline state.

Experimental

Melting points were uncorrected. The IR spectra were recorded using a Perkin-Elmer 258 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded using Varian FM 390 (90 MHz), Varian Gemini 300 (300 MHz) and Varian Gemini 200 (200 MHz) spectrometers. Mass spectra were recorded on Shimadzu QP 1000 and Hewlett Packard 5985 GC–MS spectrometers and a JEOL mass spectrometer (JMS-DX 303 HF). The absorption

Table 4 Bond lengths and bond angles for compound **2d**

(*a*) Bond lengths/Å

O1–C4	1.264(5)	C5A–C8A	1.342(6)
O2–C5	1.184(7)	C5A–C9	1.493(9)
C1–C1A	1.403(6)	C6–C7	1.511(7)
C1–C2	1.524(8)	C7–C8	1.516(8)
C1A–C4A	1.400(7)	C7–C13	1.544(9)
C1A–N10	1.476(8)	C7–C14	1.432(9)
C2–C3	1.541(7)	C8–C8A	1.620(8)
C2–C11	1.542(8)	C8A–N10	1.344(9)
C2–C12	1.611(8)	C9–C15	1.554(7)
C3–C4	1.441(7)	N10–C16	1.477(5)
C4–C4A	1.445(8)	C16–C17	1.461(7)
C4A–C9	1.527(10)	C18–O3	1.240(13)
C5–C5A	1.504(8)	C18–C17	1.187(13)
C5–C6	1.578(9)	O3–C19	1.294(12)

(*b*) Bond angles/°

C1A–C1–C2	115.1(4)	C8A–C5A–C9	121.7(4)
C1–C1A–N10	118.2(5)	C5–C6–C7	116.8(5)
C1–C1A–C4A	124.3(4)	C6–C7–C14	109.2(5)
C4A–C1A–N10	117.3(4)	C6–C7–C13	112.0(5)
C1–C2–C12	106.4(5)	C6–C7–C8	107.6(4)
C1–C2–C11	111.1(4)	C13–C7–C14	108.9(5)
C1–C2–C3	109.2(4)	C8–C7–C14	113.5(6)
C11–C2–C12	108.2(5)	C8–C7–C13	105.7(5)
C3–C2–C12	111.3(5)	C7–C8–C8A	111.8(4)
C3–C2–C11	110.7(4)	C5A–C8A–C8	120.1(4)
C2–C3–C4	112.6(4)	C8–C8A–N10	116.2(5)
O1–C4–C3	119.3(4)	C5A–C8A–N10	123.6(5)
C3–C4–C4A	122.3(5)	C4A–C9–C5A	107.9(7)
O1–C4–C4A	118.4(4)	C5A–C9–C15	114.1(4)
C1A–C4A–C4	116.5(5)	C4A–C9–C15	110.1(4)
C4–C4A–C9	122.0(5)	C1A–N10–C8A	117.7(7)
C1A–C4A–C9	121.4(5)	C8A–N10–C16	128.7(3)
O2–C5–C6	121.0(5)	C1A–N10–C16	113.5(3)
O2–C5–C5A	125.9(5)	N10–C16–C17	111.5(4)
C5A–C5–C6	113.1(5)	C18–C17–C16	142.0(7)
C5–C5A–C9	114.2(5)	O3–C18–C17	148.7(8)
C5–C5A–C8A	124.1(5)	C18–O3–C19	128.9(9)

spectra were recorded using a Hitachi-320 spectrophotometer interfaced with a PC. The fluorescence spectra were recorded using a LIS5B Perkin-Elmer fluorescence spectrophotometer. Laser studies were performed using a Quanta DCR 2Nd-YAG laser instrument. Chromatographic purifications were performed on alumina (neutral). Intensity data collection was carried out using Siemen's R3m/V at 298 K. Table 5 contains the crystallographic and data collection details. The R3m/V software is used for centering, indexing and data collection. The unit cell dimensions were obtained by a least-square fit of 22 centred reflections in the θ range 9–20°. During data collection, the intensity of three standard reflections was monitored after every 100 reflections. No decay was observed.

The structure of **2d** was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares using the SHELXL93 program.† No absorption correction was applied. The hydrogen atoms were geometrically fixed and allowed to ride on the non-hydrogen atoms (coordinates for non-hydrogen atoms are given in Table 6). At the convergence of final discrepancy indices on F were $R1 = 0.056$ and $wR2 = 0.533$ for the 741 reflections, with $F_o > 4\sigma(F_o)$ and 298 variables.

The residual positive and negative electron density in the final map was +0.25 and −0.22 e Å^{-3} respectively while the mean and max. shift/esd was 0.25 and 0.00, respectively.

Table 5 Crystal data, structure solution and refinement details

Formula	$C_{22}H_{33}NO_3$
M	359.5
Space group	$Pna2_1$
Z	4
Cell dimensions	
a/Å	14.44(2)
b/Å	9.00(2)
c/Å	15.76(3)
V/Å^3	2048(6)
D_c/g cm^{-3}	1.17
μ linear absorption coefficient/cm^{-1}	0.763
T/K	298
Crystal size/mm	0.34 × 0.30 × 0.27
Radiation	Mo-Kα ($\lambda = 0.710\,73$ Å)
Collection range	h, 0–17; k, 0–10; l, −18–0
2θ max	50.10
Scan type	$\omega/2\theta$
Unique data	1889
Unique data with $F_o^2 > 3\sigma(F_o^2)$	741
No. of variables	298
R_1	0.056
wR_2	0.533
Weighting factor w	$1/[\sigma^2(F_o^2) + (0.4698P)^2 + 3.24P]$ $[P = (F_o^2 + 2F_c^2)/3]$
Goodness of fit	0.411

Table 6 Fractional atomic coordinates for the non-hydrogen atoms of the compound **2d**

Atom	x	y	z
O1	0.3678(2)	0.3121(5)	0.3265(2)
O2	0.3663(2)	0.3222(6)	0.6439(3)
C1	0.1054(3)	0.1374(6)	0.3353(3)
C1A	0.1635(3)	0.1389(6)	0.4067(3)
C2	0.1285(4)	0.2527(7)	0.2678(3)
C3	0.2337(3)	0.2515(8)	0.2512(4)
C4	0.2871(3)	0.2575(6)	0.3283(3)
C4A	0.2530(4)	0.1988(6)	0.4077(4)
C5	0.2930(4)	0.2633(7)	0.6402(4)
C5A	0.2512(3)	0.1930(5)	0.5626(4)
C6	0.2281(4)	0.2539(8)	0.7205(4)
C7	0.1249(3)	0.2557(8)	0.7045(3)
C8	0.1029(4)	0.1284(7)	0.6449(3)
C8A	0.1658(3)	0.1342(6)	0.5599(4)
C9	0.3135(2)	0.1919(5)	0.4870(6)
N10	0.1254(2)	0.0858(4)	0.4882(5)
C11	0.0746(4)	0.2224(8)	0.1851(4)
C12	0.0950(4)	0.4106(6)	0.3049(4)
C13	0.0690(6)	0.2249(10)	0.7862(4)
C14	0.0989(4)	0.3981(7)	0.6718(4)
C15	0.3790(3)	0.0551(6)	0.4826(8)
C16	0.0499(2)	−0.0235(5)	0.4782(5)
C17	0.0856(5)	−0.1752(6)	0.4749(16)
C18	0.1552(8)	−0.2447(11)	0.4810(28)
O3	0.1953(7)	−0.3663(9)	0.4764(17)
C19	0.2815(4)	−0.3972(8)	0.4903(9)

General method (2a–g and 3a–g)

A mixture of the tetraketone (5 mmol) and amine (5 mmol) was refluxed in acetic acid for 6–7 h. The reaction mixture was cooled and poured into crushed ice. The yellow solid obtained was filtered and purified by column chromatography over alumina (neutral) and eluted with MeOH–$CHCl_3$ (1 : 2) to isolate the respective acridinedione (see Scheme 1).

10-Benzyl-3,3,6,6,9-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 2a. Yield 80%, mp 258–260 °C (Found: C, 79.28; H, 8.08; N, 3.43. $C_{25}H_{31}NO_2$ requires C, 79.54; H, 8.27; N, 3.71%); ν_{max}(KBr)/cm^{-1} 1648, 1568; δ_C($CDCl_3$) 26.03, 26.05, 31.93, 32.96, 36.56, 44.56, 52.65, 54.51, 121.06, 129.59, 131.30, 133.30, 141.64, 156.52, 194.08; m/z 362 (22% $M^+ - CH_3$).

---

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/122.

10-Allyl-3,3,6,6,9-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 2b. Yield 78%, mp 168–170 °C (Found: C, 76.6; H, 9.07; N, 4.29. $C_{21}H_{29}NO_2$ requires C, 77.0; H, 8.90; N, 4.21%); ν_{max}(KBr)/cm^{-1} 2944, 1654, 1561; δ_C($CDCl_3$) 25.74, 31.88, 32.72, 36.66, 44.07, 50.99, 54.51, 120.52, 138.32, 154.65, 194.52; *m*/*z* 327 (2%), 312 (100% $M^+ - CH_3$).

2-(3,3,6,6,9-Pentamethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydroacridin-10-yl)ethyl acetate 2c. Yield 82%, mp 158–160 °C (Found: C, 70.52; H, 8.50; N, 3.45. $C_{22}H_{31}NO_4$ requires C, 70.73; H, 8.38; N, 3.75%); ν_{max}(KBr)/cm^{-1} 2980, 1740, 1648; δ_C($CDCl_3$) 20.60, 20.79, 20.94, 27.75, 28.95, 32.43, 40.01, 42.60, 50.02, 63.30, 116.14, 116.67, 150.99, 170.21, 195.79; *m*/*z* 358 (50% $M^+ - CH_3$), 273 (100%).

10-(3-Methoxypropyl)-3,3,6,6,9-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 2d. Yield 81%, mp 190–192 °C (Found: C, 73.86; H, 9.20; N, 3.69. $C_{22}H_{33}NO_3$ requires C, 73.50; H, 9.25; N, 3.89%); ν_{max}(KBr)/cm^{-1} 2980, 1572, 1469; δ_C($CDCl_3$) 21.07, 21.40, 27.84, 29.11, 31.36, 32.42, 40.08, 41.32, 50.06, 58.79, 68.65, 116.99, 150.65, 195.82; *m*/*z* 359 (5%), 344 (100% $M^+ - CH_3$).

10-*n*-Butyl-3,3,6,6,9-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 2e. Yield 87%, mp 231–232 °C (Found: C, 76.60; H, 9.78; N, 4.20. $C_{22}H_{33}NO_2$ requires C, 76.98; H, 9.71; N, 4.08%); ν_{max}(KBr)/cm^{-1} 2988, 1641, 1571; *m*/*z* 343 (35%), 328 (100% $M^+ - CH_3$).

10-Furfuryl-3,3,6,6,9-pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 2f. Yield 78%, mp 217–219 °C (Found: C, 75.31; H, 8.17; N, 4.01. $C_{23}H_{29}NO_3$ requires C, 75.15; H, 7.96; N, 3.81%); ν_{max}(KBr)/cm^{-1} 2944, 2864, 1630, 1571; *m*/*z* 366 (45%), 352 (70% $M^+ - CH_3$).

4-(3,3,6,6,9-Pentamethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydroacridin-10-yl)benzene-1-sulfonamide 2g. Yield 78%, mp 192–194 °C (Found: C, 65.52; H, 6.52; N, 6.08. $C_{24}H_{30}N_2O_4S$ requires C, 65.13; H, 6.83; N, 6.33%); ν_{max}(KBr)/cm^{-1} 3350, 3210, 2960, 1670; *m*/*z* 427 (82% $M^+ - CH_3$).

10-Benzyl-9-propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3a. Yield 72%, mp 179–181 °C (Found: C, 76.91; H, 8.62; N, 3.61. $C_{27}H_{35}NO_2$ requires C, 76.58; H, 8.31; N, 3.32%); ν_{max}(KBr)/cm^{-1} 2940, 1630; *m*/*z* 362 (82% $M^+ - C_3H_7$).

10-Allyl-9-propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3b. Yield 85%, mp 137–139 °C (Found: C, 77.48; H, 9.52; N, 4.21. $C_{23}H_{33}NO_2$ requires C, 77.71; H, 9.30; N, 3.95%); ν_{max}(KBr)/cm^{-1} 2944, 1628, 1558; *m*/*z* 312 (100% $M^+ - C_3H_7$).

2-(9-Propyl-3,3,6,6-tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydroacridin-10-yl)ethyl acetate 3c. Yield 83%, mp 192–194 °C (Found: C, 71.48; H, 8.80; N, 3.48. $C_{24}H_{35}NO_4$ requires C, 71.71; H, 8.80; N, 3.48%); ν_{max}(KBr)/cm^{-1} 2948, 1749, 1650, 1540; *m*/*z* 401 (1%), 358 (100% $M^+ - C_3H_7$).

10-(3-Methoxypropyl)-9-propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3d. Yield 82%, mp 121–123 °C (Found: C, 74.47, H, 9.84; N, 3.45. $C_{24}H_{37}NO_3$ requires C, 74.37; H, 9.62; N, 3.61%); ν_{max}(KBr)/cm^{-1} 2950, 1640, 1530.

10-*n*-Butyl-9-propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3e. Yield 80%, mp 160–162 °C (Found: C, 77.81; H, 9.82; N, 4.01. $C_{24}H_{37}NO_2$ requires C, 77.53; H, 10.01; N, 3.71%); ν_{max}(KBr)/cm^{-1} 2944, 1634, 1521; *m*/*z* 328 (100% $M^+ - C_3H_7$).

10-*p*-Anisyl-9-propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3f. Yield 77%, mp 205–207 °C (Found: C, 77.19; H, 8.52; N, 3.48. $C_{27}H_{35}NO_3$ requires C, 76.97; H, 8.37; N, 3.32%); ν_{max}(KBr)/cm^{-1} 2940, 1638, 1540; *m*/*z* 421 (10%), 378 (100% $M^+ - C_3H_7$).

9-Propyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 3g. Yield 92%, mp 250–252 °C (Found: C, 76.21; H, 9.14; N, 4.36. $C_{20}H_{29}NO_2$ requires C, 76.10; H, 9.20; N, 4.40%); ν_{max}(KBr)/cm^{-1} 3230, 3050, 2940, 1620, 1540; *m*/*z* 272 (100% $M^+ - C_3H_7$).

Preparation of 9-phenylethyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione 4a. A mixture of dimedone (5 mmol) and hydrocinnamaldehyde (2.5 mmol) was refluxed in ethanol (40 ml) in the presence of ammonium hydroxide for 8 h. The separated yellow solid was filtered, dried and crystallised from MeOH–$CHCl_3$ (1 : 2). Yield 90%, mp 198–200 °C (Found: C, 79.61; H, 8.60; N, 4.01. $C_{25}H_{31}NO_2$ requires C, 79.50; H, 8.21; N, 3.71%); ν_{max}(KBr)/cm^{-1} 3240, 2930, 1620, 1540; *m*/*z* 377 (80%).

Acknowledgements

We thank the Department of Science and Technology and the University grants commission (New Delhi) special assistance programme for financial assistance, Dr G. Subramanian and Prof. M. L. Trudell, University of New Orleans, Dr K. J. Prabahar, Rensslaer Polytechnic Institute, New York and Dr V. Jayathirtha Rao, IICT, Hyderabad for ^1H and ^{13}C NMR spectra.

References

1 M. Maeda, *LASER Dyes*, Academic Press, New York, 1984.

2 K. J. Prabahar, V. T. Ramakrishnan, D. Sastikumar, S. Selladurai and V. Masilamani, *Indian. J. Pure Appl. Phys.*, 1991, **29**, 382.

3 P. Shanmugasundaram, K. J. Prabahar and V. T. Ramakrishnan, *J. Heterocycl. Chem.*, 1993, **30**, 1003.

4 P. Shanmugasundaram, P. Murugan and V. T. Ramakrishnan, *Heteroat. Chem.*, 1996, **7**, 17.

5 N. Srividya, P. Ramamurthy, P. Shanmugasundaram and V. T. Ramakrishnan, *J. Org. Chem.*, 1996, **61**, 5080.

6 J. Sivaraman, K. Subramanian, S. Ganesan and V. T. Ramakrishnan, *J. Biomol. Struct. Dyn.*, 1994, **13**, 119.

7 K. Gunasekaran, D. Velmurugan, P. Murugan, V. T. Ramakrishnan, K. Panneerselvam and M. Sorino Garcia, *Acta Cryst.*, *Sect. C*, 1996, **52**, 2609.

Paper 7/01401E
Received 27*th February* 1997
Accepted 19*th January* 1998