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Microwave assisted synthesis, chemiluminescent and theoretical studies of bromoalkyl esters of acridine-9-carboxylic acid

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Previously unknown esters of acridine-9-carboxylic acid have been synthesized in moderate to good yields under microwave irradiation using phase transfer catalyst aliquat. Chemiluminescent properties of the synthesized compounds have been studied using luminometer and the experimental findings are justified by theoretical studies.

Keywords: Acridine-9-carboxylic esters, microwave irradiation, chemiluminescence, aliquat, DFT

Microwave-assisted organic synthesis (MAOS) has revolutionized organic transformations and has become a powerful tool for accelerating drug discovery and development processes. Some organic reactions proceed much faster and with higher yields under microwave irradiation compared to conventional methods, even at comparable reaction temperatures. Chemiluminescent (CL) compounds are widely used in tests designed for various medical diagnoses and have shown comparable sensitivity to radio immunoassay (RIA) and enzyme immunoassay (EIA)[1]. Acridinium esters and their chemiluminescent products are strongly fluorescent and therefore they do not need any external fluorophore or any additional catalyst for chemiluminescence measurements. In immunoassays, usually the acridinium esters are first transformed into active N-hydroxysuccinimide esters (NHS-esters), which can then directly be coupled to biomolecules under very mild conditions[2]. Phenyl acridine-9-carboxylates are the precursors of chemiluminescent indicators and chemiluminogenic fragments of chemiluminescent labels, commonly applied in immunoassay tests[3]. In continuation of the search for new and analytically useful chemiluminogens, bromoalkyl acridine-9-carboxylates have been synthesized in the present report. An attempt was also made to understand the observed chemiluminescence property of bis(10*H*-acridine-9-yl-carbonyloxy)methane **3a** with the aid of DFT studies[4]. The optimized geometries of **3a**, **B**, **C** and acridone **D** molecules were obtained in gaseous phase at RT and normal pressure. Potassium salt of carboxylic acids, including a hindered acid such as mesitoic acid rapidly react with primary and secondary bromides and iodides in dipolar aprotic solvents especially hexamethylphosphoramide (HMPA) to give high yields of carboxylic esters[5]. Using phase transfer catalyst, good yields of esters have been obtained from primary, secondary, benzylic, allylic and phenacyl halides[6]. Alkylation by long-chain primary halides under microwaves has been studied[7]. Without phase transfer catalyst, in protic solvents the reaction is useful only for fairly active R, such as benzylic, allylic, *etc*. and not for tertiary alkyl since elimination occurs instead[8]. In the present work, esterification is reported in high yields by alkylation of carboxylic acid salts *via* microwave irradiation in the presence of phase transfer catalyst.

Results and Discussion

The acridine-9-carboxylic acid **1** was synthesized by irradiating a mixture of N-phenyl isatin with 10% KOH solution in microwave for 10 min at 160 W. It was also synthesized conventionally[9] by refluxing the above reaction mixture for 12 hr. Long chain bromoalkyl esters were synthesized by dibromoalkanes and acridine-9-carboxylic acid in the presence of triethylamine. The objective was synthesis of chemi-

luminescent N-methyl acridine-9-carboxylic acid ester by using methyl iodide, since N-methylation of pyridine with MeI is reported[10]. Even with excess of methyl iodide only the methyl acridine-9-carboxylate was obtained. It is obvious to state that the presence of carboxyl group at 9th position in acridine-9-carboxylic acid reduces the nucleophilicity of nitrogen preventing N-methylation. In the absence of phase transfer catalyst (PTC) the yields are limited to 4-38% with different dibromoalkanes. A significant improvement in the isolated yield of the esters was achieved when phase transfer catalyst aliquat-336 (trioctylmethyl ammonium chloride)[7] was used (**Table I**). In order to check the reaction, various dibromoalkanes have been treated with acridine-9-carboxylic acid **1** in 1:1 and 2:1 molar ratios and in all such cases the monomeric product is the major one except in the case of dibromomethane, which yielded dimer **3a** exclusively under both conditions (**Scheme I**).

Mixture of NaOH and H_2O_2 (1:1) was added in DMF solution of compounds followed by intensity measurement. Only the dimers **3** showed the chemiluminescence (**Figure 1**). The solution of dimer in DMF became deep blue immediately when NaOH and H_2O_2 mixture was added into it. The color intensity persists for about 10 sec.

Chemiluminescence involves release of light after breaking and formation of bonds. It has been proposed by Agiamarnioti *et al.*[2] that chemiluminescence in case of biotinylated acridinium esters undergo with the formation of peroxy derivative, dioxetane derivative and acridone derivative (**Scheme II**). In order to understand the detailed chemiluminescence properties of **3a**, optimized geometry of **3a**, **B**, **C** and **D** were obtained. Similarly, first, second and third excited state energies (singlet and triplet) of **D** were calculated.

First excited state energy (S_1), second excited state energy (S_2), third excited state energy (S_3), first triplet excited state energy (T_1) and corresponding oscillator strength (f) of **D** were found to be 3.47 eV (357 nm) (f=0.00); 3.67 eV (338 nm) (f=0.08); 3.73 eV (333 nm) (f=0.02); 2.71 eV (457 nm), respectively (**Table II**). Experimentally, during chemiluminescence a dark blue light was visible, which lasted for about 10 sec suggesting the possibility of phosphorescence. Thus, it seems that the molecule **D** after getting excited reaches to S_3 which then undergoes internal conversion to S_2 and S_1 and then at the end undergoes intersystem crossing to reach T_1. Finally, it emits light around wavelength 457 nm (**Figure 2**).

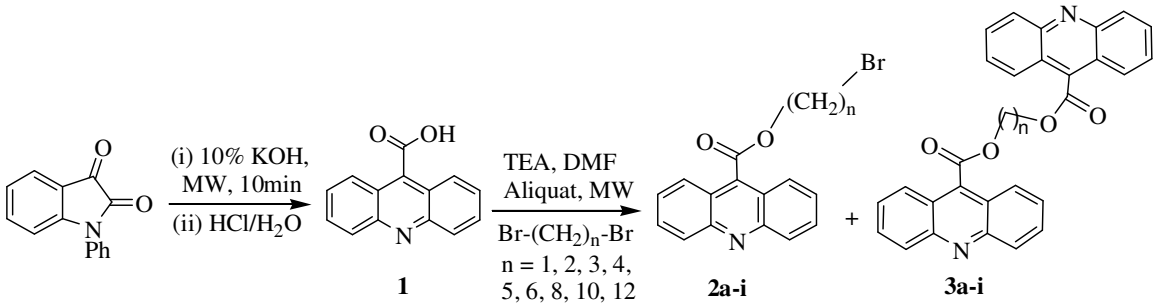
Since **D** undergoes excitation, it was pertinent to calculate the amount of energy released during the formation of **D** from the molecule **C** involving elimination of CO_2 molecule. The energy released during such a process is found to be 3.74 eV, which matches well with the S_3 energy value of D (3.73 eV). It can thus be inferred that during chemiluminescence the molecule **3a** adds OOH moiety and then undergoes transformation to **C**. The reaction involving conversion of **C** to **D** involves elimination of CO_2 molecule with the release of energy of the order 3.74 eV. This energy is utilized by **D** to reach to S_3 which then comes back to S_1 and then undergoes intersystem crossing to reach to T_1. Since the energy difference between T_1 and the ground state is calculated to be 2.71 eV (457 nm), it can be inferred that the blue light that is observed during chemiluminescence is due to the phenomenon of phosphorescence in which the molecule **D** reaches to its ground state from triplet excited state (**Figure 2**).

Computational methods

All the optimized geometries: **3a**, **B**, **C**, **D** (**Figure 3**), were calculated and obtained with DFT method. They were performed employing the B3LYP functional, which combines Becke's three-parameter exchange functional[11] and the no local correlation functional of Lee, Yang and Parr[12], together with the split-valence 6-31G basis set[13]. All the calculations were performed with Gaussian03 program[14]. In order to obtain excited state energies of **D**, TD-DFT[15,16] calculations were performed using 6-31G basis set.

Experimental Section

All chemicals were used as received from Merck or Sigma-Aldrich. The N-phenyl isatin was synthesized from diphenyl amine[10]. Microwave studies were carried out in Discover BenchMate System Make CEM, USA. All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F_{254} UV indicator). IR spectra were recorded as KBr discs on Jasco FT/IR-5300 spectrophotometer. NMR spectra were recorded in $CDCl_3$ (300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively) with TMS as an internal standard on a Jeol AL 300 FT NMR spectrometer. Chemical shifts were reported in parts per million (δ ppm). Mass spectra (MS) were recorded at 70 eV ionizing voltage on a Jeol SX-102 (FAB). Melting points were determined using a calibrated thermometer by Buchi B-540 melting point apparatus



Scheme I — Synthesis of monomers **2a-i** and dimers **3a-i**

Table I — Yields of the different esters with PTC

Entry	Dibromoalkane	**2** Yield (%)	**3** Yield (%)
1	CH_2Br_2	**2a** (6)	**3a** (68)[a]
2	$(CH_2)_2Br_2$	**2b** (62)	**3b** (15)[b]
3	$(CH_2)_3Br_2$	**2c** (64)	**3c** (16)[b]
4	$(CH_2)_4Br_2$	**2d** (72)	**3d** (12)[b]
5	$(CH_2)_5Br_2$	**2e** (68)	**3e** (14)[b]
6	$(CH_2)_6Br_2$	**2f** (60)	**3f** (11)[b]
7	$(CH_2)_8Br_2$	**2g** (53)	**3g** (10)[b]
8	$(CH_2)_{10}Br_2$	**2h** (38)	**3h** (9)[b]
9	$(CH_2)_{12}Br_2$	**2i** (36)	**3i** (10)[b]

[a]Acridine-9-carboxylic acid:dibromomethane (1:2)
[b]Acridine-9-carboxylic acid:dibromoalkanes (1:1)

and are uncorrected. LKB, Wallac, 1250 luminometer was used for the intensity measurement.

Synthesis of acridine-9-carboxylic acid, 1

A solution of N-phenylisatin (1.0 g, 6.8 mmol) in 15 mL KOH (10% aq. solution) was irradiated under microwave irradiation (160 W) at 110ºC for 10 min. After cooling to RT, the reaction mixture was poured into crushed ice when a yellow coloured solid precipitated. The precipitate was filtered, washed with chilled water, dried and recrystallized from ethanol to give pure compound (Yield 0.930 g, 93%). m.p. 287-88ºC (Lit.[9c] m.p. 289-90ºC); IR (KBr): 3436, 1660, 1606, 1461, 1288 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.73 (t, 2H, *J*=7.5 Hz), 7.93 (t, 2H, *J*=7.5 Hz), 8.08 (d, 2H, *J*=8.4 Hz), 8.22 (d, 2H, *J*=8.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 120.9, 125.3, 127.4, 129.3, 130.8, 147.9, 168.3; FAB-MS (70 eV): *m/z* 223 [M^+].

Synthesis of 3a

To a solution of acridine-9-carboxylic acid (223 mg, 1.0 mmol) in DMF (4 mL), triethylamine (0.14 mL, 1.0 mmol) was added. After shaking for 10 min, dibromomethane (0.04 mL, 0.5 mmol), trioctyl methyl ammonium chloride (0.05 mL, 0.1 mmol) were added. The reaction mixture was irradiated in microwave oven at 110ºC for 6 min. After cooling to RT the reaction mixture was poured into crushed ice and the precipitated mass was filtered and washed with chilled water. The solid obtained was purified by column chromatography using ethyl acetate and *n*-hexane (1:9), m.p. 167-68ºC, R_f = 0.4 (ethyl acetate and *n*-hexane; 1:4); IR (KBr): 1751, 1518, 1457, 1262 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.76 (s, 2H), 7.51 (t, 4H, *J*=7.8 Hz), 7.80 (t, 4H, *J*=7.2 Hz), 8.07 (d, 4H, *J*=8.7 Hz), 8.29 (d, 4H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 81.2, 122.3, 124.8, 127.6, 130.1, 134.7, 148.6, 166.2; FAB-MS (70 eV): *m/z* 458[M^+].

General procedure for synthesis of bromo alkyl esters 2b-i and dimers, 3b-i

To a solution of acridine-9-carboxylic acid (1.0 mmol) in DMF (4 mL), triethylamine (1.0 mmol) was added. After shaking the reaction mixture for 10 min, 1,ω-dibromoalkane (1.0 mmol) and trioctyl methyl ammonium chloride (0.05 mL, 0.1 mmol) were added. The reaction mixture was irradiated for 6 min. The product formation was monitored by TLC. After cooling to RT, the reaction mass was poured into crushed ice, the precipitated product was filtered and washed with chilled water. In some cases a solid product did not precipitate out. In that case the reaction mass was extracted with dichloromethane. The organic layer was washed with brine, dried over anhyd. $MgSO_4$, filtered and concentrated under vacuum to obtain the crude product. Pure products were obtained by column chromatography over silica gel.

Acridine-9-carboxylic acid 2-bromoethyl ester, 2b: yellow solid, m.p. 106-07ºC, R_f = 0.7 (ethyl acetate and *n*-hexane; 1:4); IR (KBr): 1722, 1517, 1425, 1212, 565 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.78 (t, 2H, *J*=5.7 Hz), 4.98 (t, 2H, *J*=5.7 Hz), 7.63 (t,

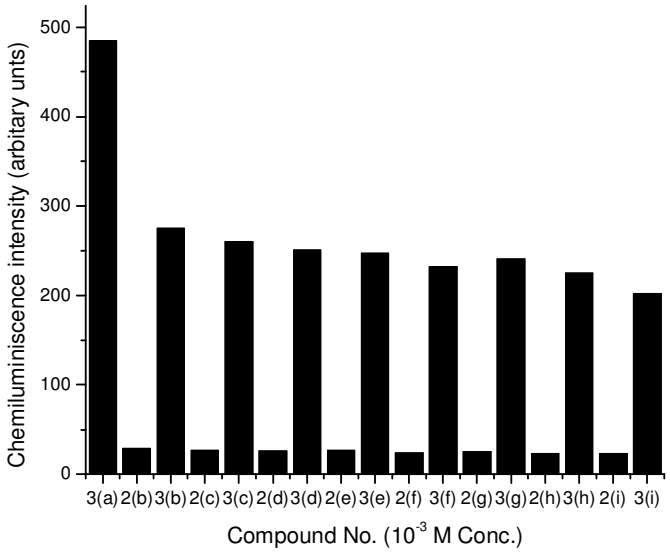
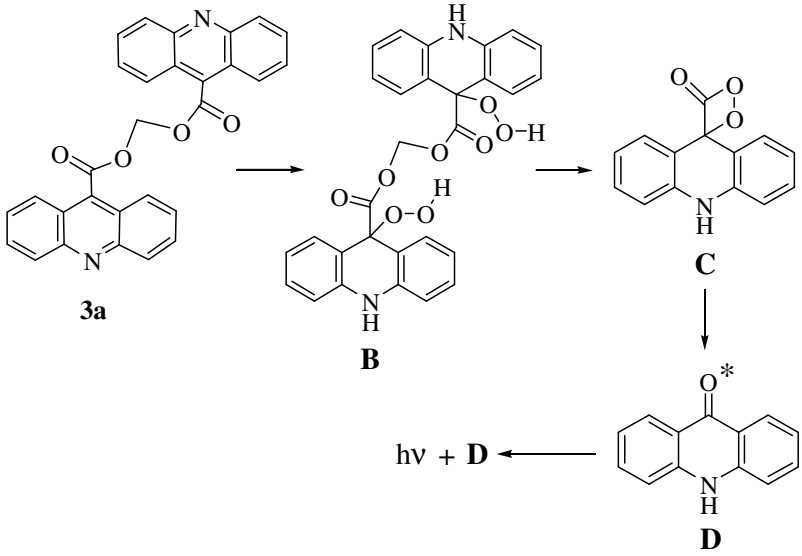


Figure 1 — Dendogram showing the chemiluminescence intensity of esters



Scheme II — Proposed light emission mechanism

2H, *J*=7.5 Hz), 7.83 (t, 2H, *J*=6.6 Hz), 8.09 (d, 2H, *J*=8.7 Hz), 8.27 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.3, 64.5, 121.3, 124.1, 126.3, 128.9, 129.3, 135.3, 147.6, 166.1; FAB-MS (70 eV): *m/z* 330.1 [M^++1].

Dimer, 3b: yellow solid, m.p. 176-77ºC, R_f = 0.2 (ethyl acetate and *n*-hexane; 1:4); IR (KBr): 1722, 1517, 1425, 1212, 565 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.18 (t, 4H, *J*=5.7 Hz), 7.63 (t, 2H, *J*=7.5 Hz), 7.84 (t, 2H, *J*=6.6 Hz), 8.03 (d, 2H, *J*=8.7 Hz), 8.20 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.5, 121.3, 124.0, 126.3, 128.7, 129.5, 13543, 14756, 166.1; FAB-MS (70 eV): *m/z* 473.2 [M^++1].

Acridine-9-carboxylic acid 3-bromopropyl ester, 2c: pale yellow solid, m.p. 104-05ºC, R_f = 0.8 (ethyl acetate and *n*-hexane; 1:4); IR (KBr): 1729, 1516, 1424, 1225, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37-2.41 (m, 2H), 3.55 (t, 2H, *J*=6.3 Hz), 4.81 (t, 2H, *J*=6.0 Hz), 7.62 (m, 2H), 7.83 (m, 2H), 8.0 (d, 2H, *J*=8.7 Hz), 8.26 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 30.2, 62.7, 121.3, 124.0, 126.2, 128.9, 129.3, 135.0, 147.6, 166.0; FAB-MS (70 eV): *m/z* 344.0 [M^++1].

Dimer, 3c: yellow solid, m.p. 181-82ºC, R_f = 0.15 (ethyl acetate and *n*-hexane; 1:4); IR (KBr): 1726, 1526, 1424, 1220, 598 cm^{-1}; ^{1}H NMR (300 MHz,

$CDCl_3$): δ 2.39-2.41 (m, 2H), 4.84 (t, 4H, *J*=6.3 Hz), 7.60 (m, 2H), 7.84 (m, 2H), 8.02 (d, 2H, *J*=8.7 Hz), 8.24 (d, 2H, *J*=8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.2, 62.9, 121.2, 124.2, 126.1, 128.8, 129.2, 135.1, 147.6, 166.3; FAB-MS (70 eV): *m/z* 487.4 [M^++1].

Acridine-9-carboxylic acid 4-bromobutyl ester, 2d: white solid, m.p. 60-62ºC, R_f = 0.8 (ethyl acetate and *n*-hexane; 1:5); IR (KBr): 1729, 1516, 1424, 1225, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17-2.22 (m, 4H), 3.48 (t, 2H, *J*=7.5 Hz), 4.69 (t, 2H, *J*=7.2 Hz), 7.62 (t, 2H, *J*=7.2 Hz), 7.83 (t, 2H, *J*=6.9 Hz), 8.01 (d, 2H, *J*=8.7 HZ), 8.26 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4, 28.2, 31.8, 64.3, 121.3, 123.9, 126.2, 128.9, 129.3, 135.8, 147.6, 166.5; FAB-MS (70 eV): *m/z* 358.2 [M^++1].

Dimer, 3d: white solid, m.p. 182-83ºC, R_f = 0.15 (ethyl acetate and *n*-hexane; 1:5); IR (KBr): 1722, 1510, 1419, 1221, 589 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22-2.29 (m, 4H), 4.74 (t, 4H, *J*=7.2 Hz), 7.60 (t, 2H, *J*=7.2 Hz), 7.81 (t, 2H, *J*=6.9 Hz), 8.10 (d, 2H, *J*=8.7 HZ), 8.24 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.6, 28.4, 64.1, 121.5, 123.9, 126.1, 128.9, 129.2, 135.8, 147.5, 166.7; FAB-MS (70 eV): *m/z* 501.0 [M^++1].

Acridine-9-carboxylic acid 5-bromopentyl ester, 2e: white solid, m.p. 55-56ºC, R_f = 0.7 (ethyl acetate and *n*-hexane; 1:6); IR (KBr): 1720, 1512, 1463, 1261, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58-1.85 (m, 6H), 3.35 (t, 2H, *J*=6.6 Hz), 4.58, (t, 2H, *J*=6.6 Hz), 7.54 (t, 2H, *J*=6.6 Hz), 7.74 (t, 2H, *J*=6.6 Hz), 7.93 (d, 2H, *J*=8.4 Hz), 8.2 (d, 2H, *J*=8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7, 26.9, 31.2, 32.3, 65.4, 121.3, 124.3, 126.1, 128.9, 129.3, 136.0, 147.6, 166.6; FAB-MS (70 eV): *m/z* 372.3 [M^++1].

Dimer, 3e: pale yellow solid, m.p. 181-82ºC, R_f = 0.15 (ethyl acetate and *n*-hexane; 1:6); IR (KBr): 1720, 1512, 1463, 1261, 597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59-1.88 (m, 6H), 4.60, (t, 4H, *J*=6.3 Hz), 7.56 (t, 2H, *J*=6.0 Hz), 7.75 (t, 2H, *J*=6.6 Hz), 7.92 (d, 2H, *J*=8.1 Hz), 8.2 (d, 2H, *J*=8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 2347, 26.9, 31.1, 65.7, 121.3, 124.3, 126.2, 128.9, 129.4, 136.1, 147.6, 166.4; FAB-MS (70 eV)): *m/z* 515.1 [M^++1].

Acridine-9-carboxylic acid 6-bromohexyl ester, 2f: white solid, m.p. 50-51°C, R_f = 0.55 (ethyl acetate and *n*-hexane; 1:8); IR (KBr): 1724, 1517, 1466, 1220, 598 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47-1.62 (m, 4H), 1.84-1.92 (m, 4H), 3.33 (t, 2H, *J*=6.6 Hz), 4.58 (t, 2H, *J*=6.3 Hz), 7.54 (t, 2H, *J*=6.9), 7.74 (t, 2H, *J*=6.3 Hz), 7.93 (d, 2H, *J*=8.7 Hz), 8.19 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.2, 26.6, 27.5, 31.5, 32.5, 65.2, 121.3, 124.0, 126.1, 128.9, 129.3, 136.1, 147.6, 166.5; FAB-MS (70 eV): *m/z* 386.1 [M^++1].

Dimer, 3f: white solid, m.p. 180-81ºC, R_f = 0.55 (ethyl acetate and *n*-hexane; 1:8); IR (KBr): 1721, 1517, 1464, 1225, 604 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45-1.61 (m, 4H), 1.84-1.96 (m, 4H), 4.62 (t, 4H, *J*=6.3 Hz), 7.54 (t, 2H, *J*=6.9), 7.76 (t, 2H, *J*=6.3 Hz), 7.94 (d, 2H, *J*=8.7 Hz), 8.21 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 26.5, 27.5,

Table II — Excited state energies and oscillator strength of **D**

Excited State	Energies of **D** (eV)	Wavelength (nm)	Oscillator Strength (f)
S_1	3.47	357	0.00
S_2	3.67	338	0.08
S_3	3.73	333	0.02
T_1	2.71	457	0.00

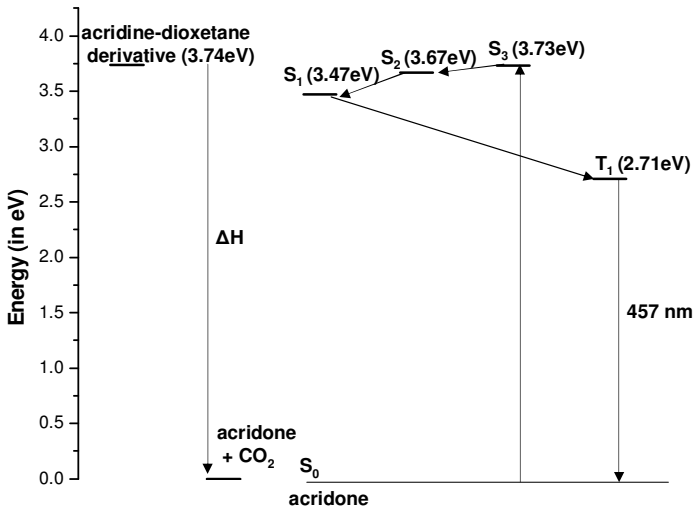


Figure 2 — Comparative energy diagram of **C**, **D** and CO_2 and excited state energies of **D**

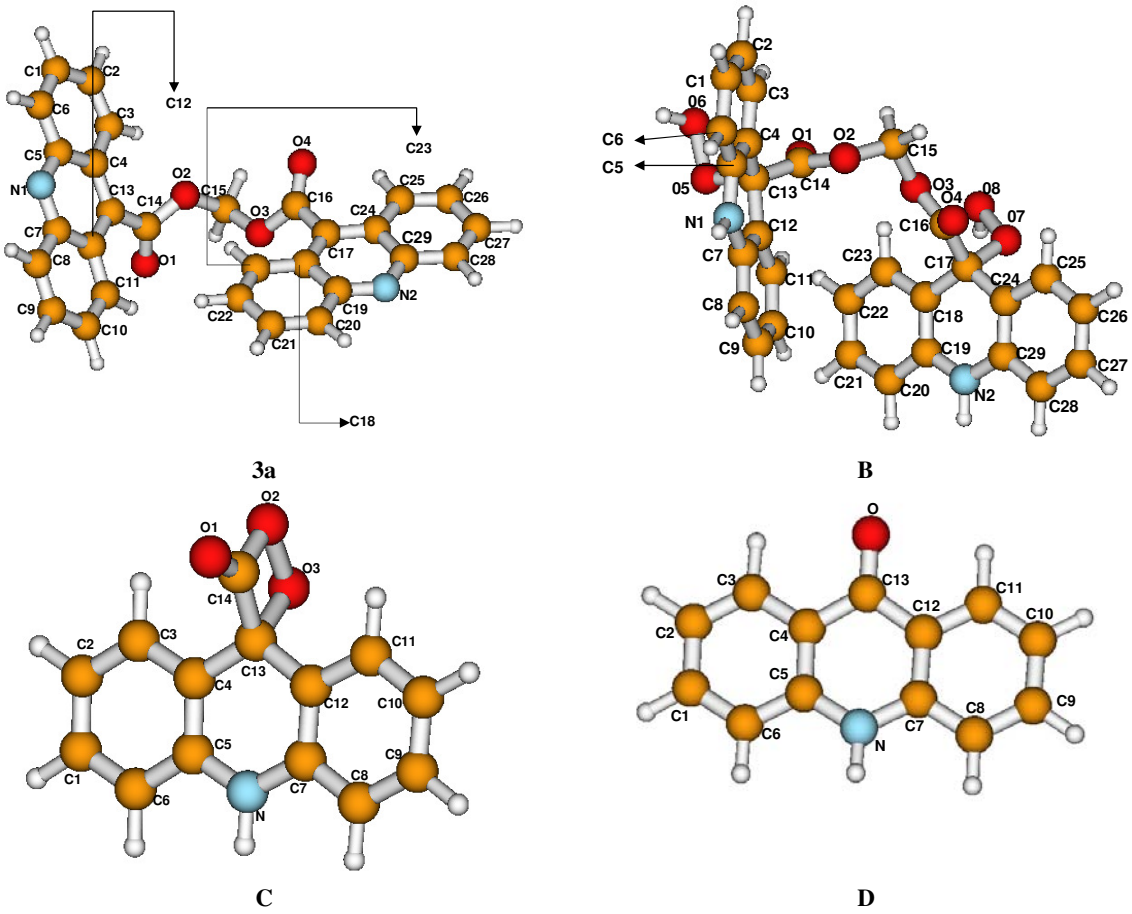


Figure 3 — (a) Optimized state geometry of bis(10*H*-acridine-9-yl-carbonyloxy)methane **3a**, (b) Optimized state geometry of **B**, (c) Optimized state geometry of acridine-dioxetane derivative **C**, (d) Optimized state geometry of acridone **D**.

31.5, 65.1, 121.2, 124.1, 126.1, 128.8, 129.3, 136.2, 147.6, 166.8; FAB-MS (70 eV): *m/z* 529.1 [M^++1].

Acridine-9-carboxylic acid 8-bromooctyl ester, 2g: oily liquid, R_f = 0.6 (ethyl acetate and *n*-hexane; 1:8); IR (Nujol): 1724, 1516, 1458, 1218, 639 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29-1.59 (m, 8H), 1.79-1.89 (m, 4H), 3.57 (t, 2H, *J*=6.6 Hz), 4.57 (t, 2H, *J*=6.6 Hz), 7.53 (t, 2H, *J*=7.5 Hz) 7.74 (t, 2H, *J*=6.9 HZ), 7.93 (d, 2H, *J*=8.7 Hz), 8.18 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 22.8, 24.1, 26.6, 27.4, 31.4, 32.5, 65.1, 121.4, 124, 126.2, 129.1, 129.4, 136.2, 147.6, 166.6; FAB-MS (70 eV)): *m/z* 414.4 [M^++1].

Dimer, 3g: yellow solid, m.p. 177-78ºC, R_f = 0.25 (ethyl acetate and *n*-hexane; 1:8); IR (KBr): 1722, 1516, 1462, 1218, 645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33-1.55 (m, 8H), 1.81-1.91 (m, 4H), 4.61 (t, 4H, *J*=6.6 Hz), 7.51 (t, 2H, *J*=7.5 Hz) 7.76 (t, 2H, *J*=6.9 HZ), 7.90 (d, 2H, *J*=8.7 Hz), 8.15 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2, 22.7, 24.1, 26.6, 27.4, 31.7, 65.3, 121.4, 124.1, 126.3, 129.1, 129.3, 136.1, 147.6, 166.4; FAB-MS (70 eV): *m/z* 557.1 [M^++1]

Acridine-9-carboxylic acid 10-bromodecyl ester, 2h: oily liquid, R_f = 0.63 (ethyl acetate and *n*-hexane; 1:8); IR (Nujol): 1725, 1515, 1457, 1221, 641 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39-1.59 (m, 10H), 1.86-1.92 (m, 4H), 2.17-2.22 (m, 2H), 3.39 (t, 2H, *J*=6.9 Hz), 4.64 (t, 2H, *J*=6.6 Hz), 7.60 (t, 2H, *J*=7.5 Hz), 7.81 (t, 2H, *J*=7.2 Hz), 8.0 (d, 2H, *J*=8.4 Hz), 8.25 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 22.1, 22.3, 22.8, 24.1, 26.5, 27.4, 31.3, 32.5, 65.2, 121.4, 124.1, 126.3, 129.1, 129.4, 136.3, 147.5, 166.6; FAB-MS (70 eV): *m/z* 442.0 [M^++1].

Dimer, 3h: pale yellow solid, m.p. 179-80°C, R_f = 0.25 (ethyl acetate and *n*-hexane; 1:8); IR (KBr): 1723, 1518, 1459, 1226, 641 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39-1.59 (m, 10H), 1.86-1.92 (m, 4H), 2.17-2.22 (m, 2H), 4.69 (t, 4H, *J*=6.6 Hz), 7.62 (t, 2H, *J*=7.5 Hz), 7.80 (t, 2H, *J*=7.2 Hz), 8.07 (d, 2H,

J=8.4 Hz), 8.24 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 22.1, 22.3, 22.7, 24.2, 26.5, 27.7, 31.5, 65.2, 121.4, 124.1, 126.3, 129.1, 129.3, 136.3, 147.7, 166.9; FAB-MS (70 eV): *m/z* 585.1[M^++1].

Acridine-9-carboxylic acid 12-bromododecyl ester, 2i: oily liquid, R_f = 0.66 (ethyl acetate and *n*-hexane; 1:8); IR (Nujol): 1723, 1514, 1459, 1224, 644 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21-1.57 (m, 16H), 1.82-1.91 (m, 4H), 3.33 (t, 2H, *J*=6.6 Hz), 4.57 (t, 2H, *J*=6.9 Hz), 7.53 (t, 2H, *J*=7.5 Hz), 7.74 (t, 2H, *J*=7.2 Hz), 7.94 (d, 2H, *J*=8.7 Hz), 8.18 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 22.1, 22.3, 22.9, 24.1, 26.6, 27.5, 31.4, 32.5, 66.2, 121.5, 124.2, 126.4, 129.1, 129.5, 136.4, 147.6, 166.7; FAB-MS (70 eV): *m/z* 470.5 [M^++1].

Dimer, 3i: pale yellow solid, m.p. 182-83°C, R_f = 0.2 (ethyl acetate and *n*-hexane; 1:8); IR (KBr): 1723, 1510, 1459, 1210, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23-1.59 (m, 16H), 1.82-1.96 (m, 4H), 4.62 (t, 4H, *J*=6.6 Hz), 7.53 (t, 2H, *J*=7.5 Hz), 7.74 (t, 2H, *J*=7.5 Hz), 7.94 (d, 2H, *J*=8.4 Hz), 8.18 (d, 2H, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 22.0, 22.2, 22.9, 24.2, 26.7, 27.4, 31.5, 66.2, 121.5, 124.2, 126.4, 129.2, 129.4, 136.4, 147.7, 166.6; FAB-MS (70 eV): *m/z* 613.3 [M^++1].

Conclusion

Synthesis of acridine-9-carboxylic acid and its subsequent esterification was carried out in good yield by microwave irradiation using PTC. The use of simple starting materials, moderate to good yields, short reaction time and easy purification procedure present the notable advantages of this method. Chemiluminescence test was done for all acridine-9-carboxylic esters with luminometer, but it was observed in the case of dimers only. The DFT study of the dimer **3a** and its intermediate was carried out to correlate the observed chemiluminescence with the theoretical findings, and the theoretical studies were found in good agreement with the experimental values and observations.

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