

Study of Fluorescence Quenching on Novel Coumarin Derivatives by Aniline in Different Solvents

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Abstract The steady-state fluorescence quenching of novel coumarin derivatives; 4-(2, 6-dibromo-4-methyl-phenoxy-methyl)-benzo[h]chromen-2-one [DMB] and 6-methoxy-4-*p*-toloxymethyl-chromen-2-one [TMC] has been studied in toluene, benzene, dioxane, acetonitrile and tetrahydrofuran [THF] using aniline as a quencher at room temperature with a view to understanding the role of diffusion in the quenching mechanism. The probability of quenching per encounter (p) is calculated in all the solvents. Further, an activation energy for quenching (E_a) was estimated using the values of p and the literature values of activation energy for diffusion (E_d). The magnitudes of these parameters indicate that the fluorescence quenching of these molecules by aniline is not solely due to the material diffusion but there is also a contribution of an activation energy.

Keywords Activation energy · Coumarin derivative · Fluorescence quenching · Material diffusion · Stern–Volmer plot

1 Introduction

The fluorescence quenching of organic molecules in solvents by various quenchers such carbon tetrachloride, aniline, oxygen, halide ions and titanium dioxide nanoparticles has been a subject of continued investigation for the last two decades [1–5]. One of the well-known experimental techniques used to study the role of fluorescence quenching is to determine the quenching rate parameters using the Stern–Volmer [S–V] equation:

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$$\frac{I_0}{I} = 1 + K_{S-V}[Q] \quad (1)$$

where I_0 and I are the fluorescence intensities without and with quencher, respectively. K_{S-V} is the S–V constant and $[Q]$ is the quencher concentration. The S–V constant K_{S-V} can be estimated from the slope of the linear plot of I_0/I versus $[Q]$ and is equal to $k_q\tau_0$ in which k_q is the S–V quenching rate parameter and τ_0 is the fluorescence lifetime of the solute in the absence of quencher.

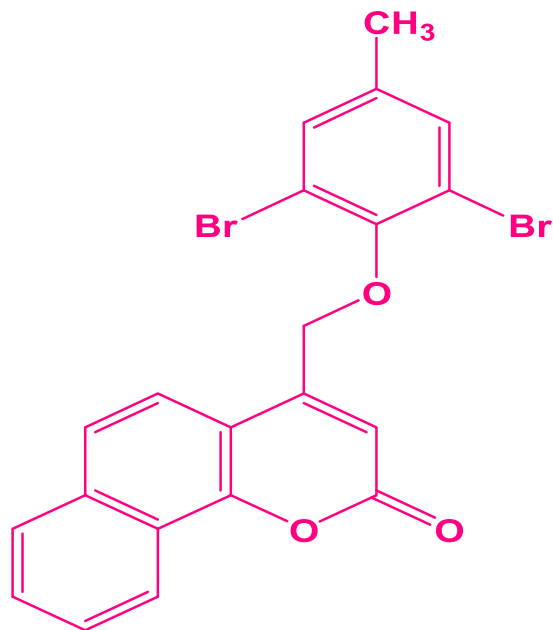
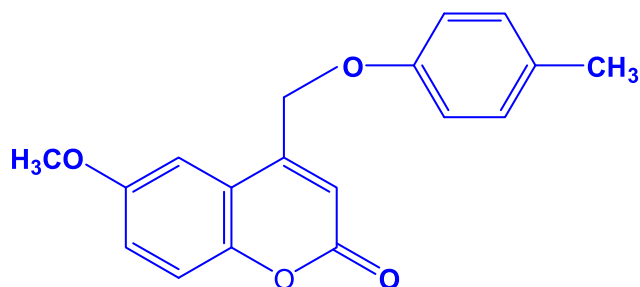
Derivatives of coumarin are well known for their photochemical and photophysical properties, as well as for their interesting second-order nonlinearities [6]. They are extensively studied due to their widespread industrial use in dye lasers [7]. Nowadays there has been a drive to synthesize coumarin based organic dyes for use in high-efficiency dye-sensitized solar cells (DSCs) [8, 9]. Coumarin and its derivatives have also attracted significant interest in pharmaceutical research fields because of their antiviral, anti-inflammatory, anticarcinogenic, hepatoprotective and anticoagulant activities [10, 11]. The iodinated-4-aryloxymethyl coumarins, which are similar to the investigated molecules, are potent anti-cancer and anti-mycobacterial agents [12]. Basanagouda et al. reported, that 4-aryloxymethyl coumarins has potent antimicrobial activity [13] and it has been reported that the investigated molecules were moderate to good as antibacterial activity against *Klebsiella pneumonia* and *Streptococcus faecalis* and as antifungal against *Penicillium notatum* and *Rhizopus*. Recently, we studied the spectroscopic properties of TMC molecules [14].

In the present work, the fluorescence quenching of the coumarin derivatives; 4-(2,6-dibromo-4-methyl-phenoxy-methyl)-benzo[h]chromen-2-one [DMB] and 6-methoxy-4-*p*-toloxy-methyl-chromen-2-one [TMC] molecules by aniline in toluene, benzene, dioxane, acetonitrile and THF solvents has been studied with a view to understanding the role of the activation energy in the quenching mechanism.

2 Materials and Methods

The coumarin derivatives 4-(2,6-dibromo-4-methyl-phenoxy-methyl)-benzo[h]chromen-2-one [DMB] and 6-methoxy-4-*p*-toloxy-methyl-chromen-2-one [TMC] were synthesized according to the literature [15]. The molecular structures of DMB and TMC are shown in Figs. 1 and 2, respectively. The fluorescence quantum yields for DMB and TMC molecules in ethanol are 20 and 23%, respectively. Toluene, benzene, dioxane, acetonitrile and THF were of spectroscopic grade and were obtained from S.D Fine Chemicals Ltd., India. Aniline was doubly distilled and tested for its purity before use. The solutions were prepared to keep the concentration of solute fixed ($5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) and varying quencher concentrations (0.00–0.10 $\text{mol}\cdot\text{L}^{-1}$) in all solvents.

The absorption spectra were recorded using the UV-visible spectrophotometer [model: Hitachi U-3310 at USIC, K U Dharwad, India] and fluorescence spectra were recorded in absence and presence of the quencher using a fluorescence spectrophotometer [model: Hitachi F-7000 at USIC, K U Dharwad, India]. The fluorescence lifetimes were recorded in the absence of the quencher using a time-correlated single photon counting technique [TCSPC ISS model: 90021 at USIC, K U Dharwad, India]. All these spectroscopic measurements were carried out at room temperature [298 K]. The experimental values are reproducible within 5% of experimental error.

Fig. 1 The molecular structure of DMB**Fig. 2** The molecular structure of TMC

3 Results and Discussion

The fluorescence intensity I_0 was measured without the quencher and then the fluorescence intensity I was measured at different quencher concentrations for DMB and TMC molecules. The fluorescence intensity decreases with addition of aniline, perhaps due to electron transfer from aniline to the investigated molecules. The S–V plots for DMB and TMC molecules were found to be linear with intercepts nearly unity; these are shown in Figs. 3 and 4. This indicates that fluorescence quenching follows the S–V relation. The slope of the S–V plots, which give the dynamic quenching constant (K_{S-V}), were determined using the least square fitting method. The fluorescence quenching rate parameter (k_q) is calculated using the experimental values of K_{S-V} and τ_0 and is given by Eq. 2.

$$k_q = \frac{K_{S-V}}{\tau_0} \quad (2)$$

The values of K_{S-V} and k_q for DMB and TMC molecules in different solvents are shown in Tables 1 and 2, respectively.

The diffusion co-efficient for solute (D_S) and for quencher (D_Q) can be estimated using the Stoke's Einstein equation [16]:

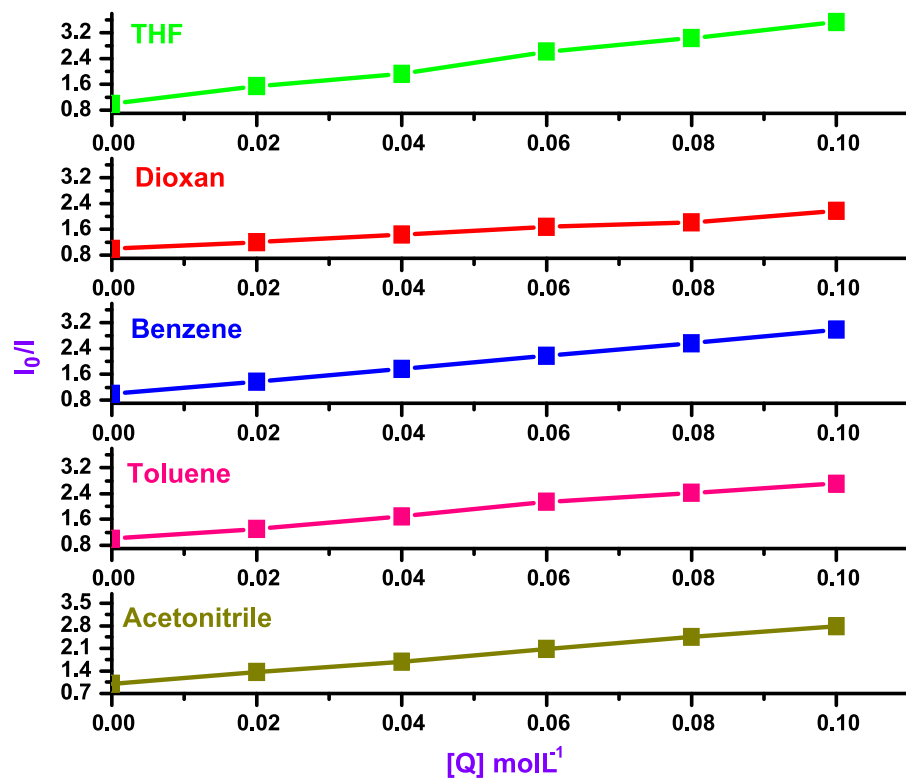


Fig. 3 The S-V plots $\{[I_0/I]$ versus aniline concentration $[Q]$ in different solvents for $C(\text{DMB}) = 5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$

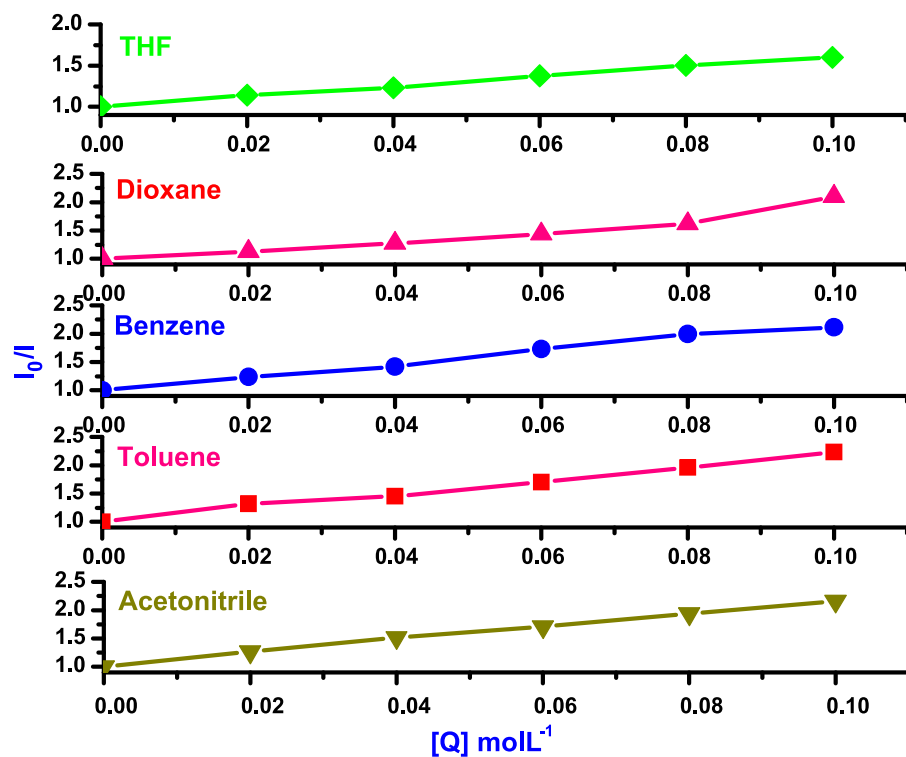


Fig. 4 The S-V plots $\{[I_0/I]$ versus aniline concentration $[Q]$ in different solvents for $C(\text{TMC}) = 5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$

Table 1 The values of S–V constant (K_{S-V}) and quenching rate parameter (k_q) for DMB molecule in different solvents

Molecule	Solvent	K_{S-V} (mol ⁻¹)	$k_q \times 10^{-9}$ (mol ⁻¹ ·s ⁻¹)
DMB	THF	17.72	1.624
	Dioxane	09.06	0.831
	Benzene	17.02	1.561
	Toluene	17.71	1.625
	Acetonitrile	25.40	2.330

Table 2 The values of S–V constant (K_{S-V}) and quenching rate parameter (k_q) for TMC molecule in different solvents

Molecule	Solvent	K_{S-V} (mol ⁻¹)	$k_q \times 10^{-9}$ (mol ⁻¹ ·s ⁻¹)
TMC	THF	05.85	0.513
	Dioxane	07.55	0.662
	Benzene	11.66	1.022
	Toluene	11.65	1.140
	Acetonitrile	11.10	0.973

$$D = \frac{KT}{a\pi\eta R} \quad (3)$$

where K , T and η are the Boltzmann constant, temperature and viscosity of the solvent respectively and ‘ a ’ is the Stoke’s Einstein number $a = 6$ for solute and $a = 3$ for quencher [17], since the radii of the solute molecules are larger than the solvent molecule. $R = R_S + R_Q$ is the sum of the radii of solute and quencher and these values were estimated using the method as suggested by Edward [18]. The values of radius of the solute, radius of quencher, sum of the radii of solute and quencher and the life time of the solutes without quencher for DMB and TMC molecules are shown at the bottom of Tables 3 and 4, respectively. Thus, using the measured values of radii and the literature values of viscosity of the respective solvent, the diffusion coefficient for D_S and D_Q for DMB and TMC molecules and for quencher molecule were calculated using the Eq. 3 and these values are shown in Tables 3 and 4, respectively. In this, the viscosity of the solute and the quencher are taken as equal to the viscosity of the medium, since their concentrations are very small. Thus, using the values of R and D , the values of k_d for DMB and TMC molecules were estimated using the Eq. 4 and these values also shown in Tables 3 and 4, respectively.

$$k_d = 4\pi N' DR \left[1 + \frac{R}{(2D\tau_0)^{1/2}} \right] \quad (4)$$

where N' is Avogadro’s number per millimole.

Further, the value of probability of quenching per encounter (p) was estimated using the Eq. 5:

$$p = \frac{k_q}{k_d} \quad (5)$$

The value of p for DMB and TMC molecules in all five solvents are also shown in Tables 3 and 4, respectively. From Tables 3 and 4, it is observed that the probability of quenching per encounter is less than unity, a fact hitherto observed by other researchers

Table 3 The inverse values of viscosity of the solvents (η^{-1}), diffusion coefficient of solute (D_S), quencher (D_Q) and sum of the diffusion coefficient of solute and quencher (D), diffusion rate parameter (k_d), probably of quenching per encounter (p), activation energy for diffusion (E_d) and activation energy for quencher (E_a) for the DMB molecule

Molecule	Solvent	$\eta^{-1} \times 10^{-2}$ P^{-1}	$D_S \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$D_Q \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$D \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$k_d \times 10^{-9}$ $(\text{mol}^{-1} \cdot \text{s}^{-1})$	p	E_d $(\text{kJ} \cdot \text{mol}^{-1})$	E_a $(\text{kJ} \cdot \text{mol}^{-1})$
DMB	THF	2.77	0.649	1.958	2.607	14.05	0.174	15.82	3.51
	Dioxane	2.22	0.438	1.289	2.727	9.249	0.088	12.80	3.64
	Benzene	1.66	0.721	2.578	3.299	18.46	0.084	12.55	4.06
	Toluene	1.81	0.787	2.811	3.598	20.21	0.080	11.13	3.72
	Acetonitrile	1.77	1.425	4.297	5.722	30.84	0.075	8.05	4.52

For the DMB molecule: $R_S = 4.28 \text{ \AA}$, $R_Q = 2.84 \text{ \AA}$, $R = R_S + R_Q = 7.12 \text{ \AA}$, $\tau_0 = 1.09 \text{ ns}$

Table 4 The inverse values of viscosity of the solvents (η^{-1}), diffusion coefficient of solute (D_S), quencher (D_Q) and sum of the diffusion coefficient of solute and quencher (D), diffusion rate parameter (k_d), probably of quenching per encounter (p), activation energy for diffusion (E_d) and activation energy for quencher (E_a) for the TMC molecule

Molecule	Solvent	$\eta^{-1} \times 10^{-2}$ P^{-1}	$D_S \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$D_Q \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$D \times 10^5$ $(\text{cm}^2 \cdot \text{s}^{-1})$	$k_d \times 10^{-9}$ $(\text{mol}^{-1} \cdot \text{s}^{-1})$	p	E_d $(\text{kJ} \cdot \text{mol}^{-1})$	E_a $(\text{kJ} \cdot \text{mol}^{-1})$
TMC	THF	2.77	0.548	2.24	2.788	16.66	0.022	15.82	4.94
	Dioxane	2.22	0.438	1.51	1.948	11.68	0.056	12.80	4.64
	Benzene	1.66	0.721	2.95	3.671	21.98	0.046	12.55	4.56
	Toluene	1.81	0.787	2.80	3.587	21.48	0.053	11.13	3.77
	Acetonitrile	1.77	1.203	4.91	6.113	36.65	0.026	8.03	4.48

For the TMC molecule: $R_S = 5.07 \text{ \AA}$, $R_Q = 2.84 \text{ \AA}$, $R = R_S + R_Q = 7.91 \text{ \AA}$, $\tau_0 = 1.14 \text{ ns}$

[19, 20]. This fact may also reflect the activation energy of a process other than the material diffusion. In a liquid system, in order to study the role of the activation process the values of activation energy for diffusion (E_d) and activation energy for quencher (E_a) are needed. Since p is related to activation energies, the following equation is used for the estimation of activation energy. The values of E_a for DMB and TMC molecules in different solvents were calculated using Eq. 6 and these values are shown in Tables 3 and 4, respectively

$$E_a = E_d + RT \ln\left(\frac{1}{p} - 1\right) \quad (6)$$

where R is the gas constant and T is the temperature in Kelvin.

It is clear from Tables 3 and 4 that the values of E_a are less than those of E_d in all the solvents studied, indicating that in the bimolecular quenching reaction the influence of diffusion process is greater than that of the quenching process.

4 Conclusion

From the foregoing discussion, we observed that the DMB and TMC molecules undergo fluorescence quenching by aniline. The fluorescence intensities of the molecules decrease with addition of aniline, perhaps due to electron transfer from aniline to the investigated molecules. The S–V plots were found to be linear in all the solvents studied. The value of the probability of quenching per encounter is less than unity in all the solvents. The activation energy for the quenching process is smaller than that for diffusion, in all the solvents. This may imply that fluorescence quenching of DMB and TMC molecules by aniline in different solvents is not solely due to material diffusion.

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References

1. Behera, P.K., Mishra, A.K.: Static and dynamic model for 1-naphthol fluorescence quenching by carbon tetrachloride in dioxane–acetonitrile mixtures. *J. Photochem. Photobiol. A: Chem.* **71**, 115–118 (1993)
2. Desai, V.R., Hunagund, S.M., Basanagouda, M., Kadadevarmath, J.S., Thipperudrappa, J., Sidarai, A.H.: Spectroscopic studies on newly synthesised 5-(2-hydroxy-5-methoxy-phenyl)-2-phenyl-2H-pyridazin-3-one molecule. *J. Mol. Liq.* **225**, 613–620 (2016)
3. Olmsted, J.: Oxygen quenching of fluorescence of organic dye molecules. *J. Chem. Phys. Lett.* **26**, 33–36 (1974)
4. Schizuka, H., Saito, T., Morita, T.: Fluorescence quenching of aromatic molecules by inorganic anions. *J. Chem. Phys. Lett.* **56**, 519–522 (1978)
5. Desai, V.R., Hunagund, S.M., Pujar, M.S., Basanagouda, M., Kadadevarmath, J.S., Sidarai, A.H.: Spectroscopic interactions of titanium dioxide nanoparticles with pharmacologically active 3(2H)-pyridazinone derivative. *J. Mol. Liq.* **233**, 166–172 (2017). doi:[10.1016/j.molliq.2017.03.018](https://doi.org/10.1016/j.molliq.2017.03.018)
6. Mortazavi, M.A., Kowel, S.T., Henry, R., Hoover, A., Lindsay, G.A.: Second-order nonlinear optical properties of poled coumaromethacrylate copolymers. *Appl. Phys. B: Lasers Opt.* **53**, 287–295 (1991)
7. Duarte, F.J., Hillman, L.W.: *Dye Laser Principles with Applications*. Academic Press Inc., San Diego (1990)
8. Kohjiro, H., Dan-oh, Y., Kasada, C., Shinpo, A., Suga, S., Sayama, K., Arakawa, H.: Design of new coumarin dyes having thiophene moieties for highly efficient organic-dye-sensitized solar cell. *New J. Chem.* **27**, 783–785 (2003)

9. Mishra, A.: Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. *Chem. Int. Ed.* **48**, 2474–2499 (2009)
10. Zhao, H., Hong, N., Mazumder, H., Wang, A., Sunder, S., Milne, S.G., Pommier, Y., Burke, T.R.: Hydrazide-containing inhibitors of HIV-1 integrase. *J. Med. Chem.* **40**, 242–249 (1997)
11. Kontogiorgis, C., Hadjipavlou, D.: Biological evaluation of several coumarin derivatives designed as possible anti-inflammatory/antioxidant agents. *J. Enzym. Inhib. Med. Chem.* **18**, 63–69 (2003)
12. Basanagouda, M., Kulkarni, M.V., Sharma, D., Gupta, V.K., Pranasha, P.: Sandhyarani, Rasal, V.P.: synthesis of some new 4-aryloxymethylcoumarins and examination of their antibacterial and antifungal activities. *J. Chem. Sci.* **121**, 485–495 (2009)
13. Basanagouda, M., Jambagi, V.B., Barigheid, N.N., Laxmeshwar, S.S., Devaru, V.: Narayanachar: synthesis, structure activity relationship of iodinated-4-aryloxymethyl-coumarins as potential anti-cancer and antimycobacterial agents. *Eur. J. Med. Chem.* **74**, 225–233 (2014)
14. Sidarai, A.H., Desai, V.R., Hunagund, S.M., Basanagouda, M., Kadadevarmath, J.S.: Effect of solvent polarity on the fluorescence quenching of TMC molecule by aniline in benzene–acetonitrile mixtures. *Can. J. Phys.* **94**, 1125–1132 (2016)
15. Basanagouda, M.: Synthesis of some new 4-aryloxymethylcoumarins and examination of their antibacterial and antifungal activities. *J. Chem. Sci.* **121**, 485–495 (2009)
16. Einstein, A.: *Investigations on the Theory of Brownian Movement*. Dover, New York (1956)
17. Kadadevarmath, J.S., Giraddi, T.P., Malimath, G.H., Chikkur, G.C.: Electronic excitation energy quenching of an organic liquid scintillator by carbon tetrachloride in different solvents. *J. Radiat. Meas.* **26**, 117–118 (1996)
18. Edward, J.T.: Molecular volumes and the Stokes–Einstein equation. *J. Chem. Edu.* **47**, 261 (1970)
19. Biradar, D.S., Thipperudrappa, J., Hanagodimath, S.M.: Fluorescence quenching studies of 1,3-diphenyl benzene. *Spectrosc. Lett.* **40**, 559–571 (2007)
20. Melavanki, R.M., Patil, N.R., Patil, H.D., Kusanur, R.A., Kadadevaramath, J.S.: Fluorescence quenching of 1, 4-bis [2-(2-methyl phenyl) ethenyl]-benzene by aniline in benzene–acetonitrile. *Indian J. Pure Appl. Phys.* **49**, 748–753 (2011)