

Photoprocesses Behavior Of Some Biologically Active Bis-Oxadiazole Compounds

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Abstract

The behavior of the absorption and fluorescence emission processes for some bis-1, 3, 4-oxadiazole sulphonyl compounds were studied in toluene, ethanol and di-methyl sulfoxide solvents. Fluorescence quenching processes of the compound bis- [2, 2'-5 ethyl sulphonyl-1, 3,4-oxadiazole]-1,4-butane, (4-Et), in toluene and ethanol using benzonitrile and benzophenone quenchers were studied too. The complex quenching mechanism of 4-Et by benzophenone, according to the obtained data, was proposed.

- 4,3,1,

(4-Et) 4,1- [- 4,3,1 - - 5 - 2'2]

(4-Et)

Introduction

1, 3, 4-oxadiazole compounds received a growing interest due to their bactericidal, fungicidal and other activities^(1,2). A great number of 1,3,4-oxadiazole derivatives have been synthesized and tested for their biological

activities^(3,4). The fluorescence and absorption behavior of some of these compounds were investigated in different solvents⁵. The structural and substitution effects on the photoprocesses were investigated, as well as their fluorescence self-quenching process and the singlet

excited state energy^{6,7}. A new derivatives of the bis-1, 3,4-oxadiazole sulphones were synthesized. These are bis [2,2'-(5-alkyl sulphonyl-1, 3,4-oxadiazole)]-1,4-butane and bis [2,2'-(5-alkyl sulphonyl-1, 3,4-oxadiazole)]-1,8-octane.⁸

In this work our interest is to study the change in the behavior of the absorption and fluorescence of these new compounds in the absence and presence of quenchers in various solvents.

Experimental

Materials: The sulphonyl oxadiazole compounds and their derivatives were synthesized and their physical properties were

studied. These derivatives were a generous gift of Prof...M.Mahmoud and I.F.Mustafa (Chem. Dept., Ibn Al-Haitham college of education) and shown in Figure-1- are :

1- Bis [2, 2'-5-methyl sulphonyl-1, 3, 4-oxadiazole] - 1, 4- butane ; (4-*Me*)

2- Bis [2,2'-5-ethyl sulphonyl-1,3,4-oxadiazole]-1,4-butane ; (4-*Et*)

3- Bis [2,2'-5-benzoyl sulphonyl-1,3,4-oxadiazole]-1,4- butane ; (4-*Ben.*)

4- Bis [2, 2'-5-methyl sulphonyl-1, 3, 4-oxadiazole] - 1,8- octane ; (8-*Me*)

5- Bis [2, 2'-5- ethyl sulphonyl-1, 3, 4-oxadiazole] -1, 8 -octane ; (8-*ET*)

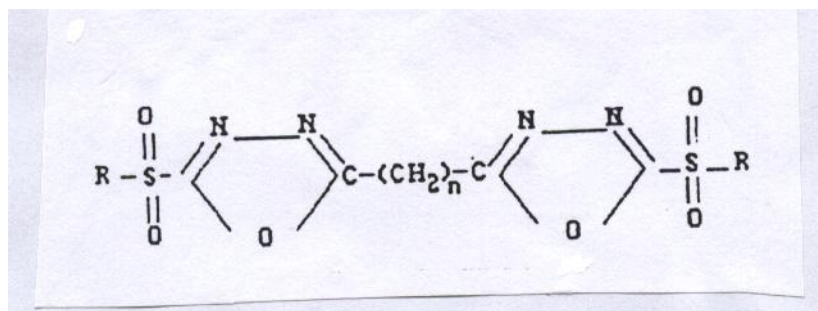


Figure-1- Structure of the Bis-Oxadiazole compounds ;

4-*Me* , 2 – 4-*Et* , 3 – 4-*Ben* ,

4 – 8-*ME* , 5 – 8-*Et* .

1 - n = 4 , R = CH₃

2 - n = 4 , R = C₂H₅

3 - n = 4 , R = CH₂ -ph

4 - n = 8 , R = CH₃

5 - n = 8 , R = C₂H₅

Toluene, ethanol (spectroscopic) and DMSO solvents from BDH are used without further purification. Benzophenone and benzonitrile are used as quenchers of oxadiazole fluorescence.

Spectroscopic measurements:

Fluorescence excitation spectra, fluorescence emission spectra and fluorescence quenching measurements are carried out using JASCO -770 spectrofluorometer at room temperature. The solutions used are of concentrations of 10^{-3} and 10^{-4} M for absorption and fluorescence measurements respectively. Fluorescence quenching data are treated using Stern-Volmer equation:

$$F_0 / F = 1 + K_{SV} [Q]$$

Where F_0 & F are the fluorescence intensity of the compounds in the absence and presence of quencher. K_{SV} is the Stern-Volmer rate constant and is

equal to $k_q \tau$; k_q is the quenching rate constant, τ is the life time of the singlet excited state. $[Q]$ is the quencher concentration.

Results and Discussion

Excitation processes

Table-1- explores the spectroscopic data of the excitation wavelength of the maximum absorption of the oxadiazole compounds in toluene, ethanol and DMSO solvents. In toluene the maximum peak is red shifted in changing the alkyl group in the 5-position from methyl to ethyl to benzyl as shown in Figure 2-. This substitution effect is observed clearly in the variation of the energy of the first excited singlet state E_{S_1} for the studied compounds listed in Table-2-. The energy of the S_1 state ($n\pi^*$) decreases as we change the end group from CH_3 to C_2H_5 to $CH_2C_6H_5$.

Table 1: Excitation wavelength (nm) of the bis-Oxadiazole compounds in different solvents

Compound	Toluene λ_{ext} nm	Ethanol λ_{ext} nm	DMSO λ_{ext} nm
4-Me	290	298	309
4-Et	310	294	312
4-Ben	338	333	-----
8-Me	355	295	-----
4-Et	315	291	-----

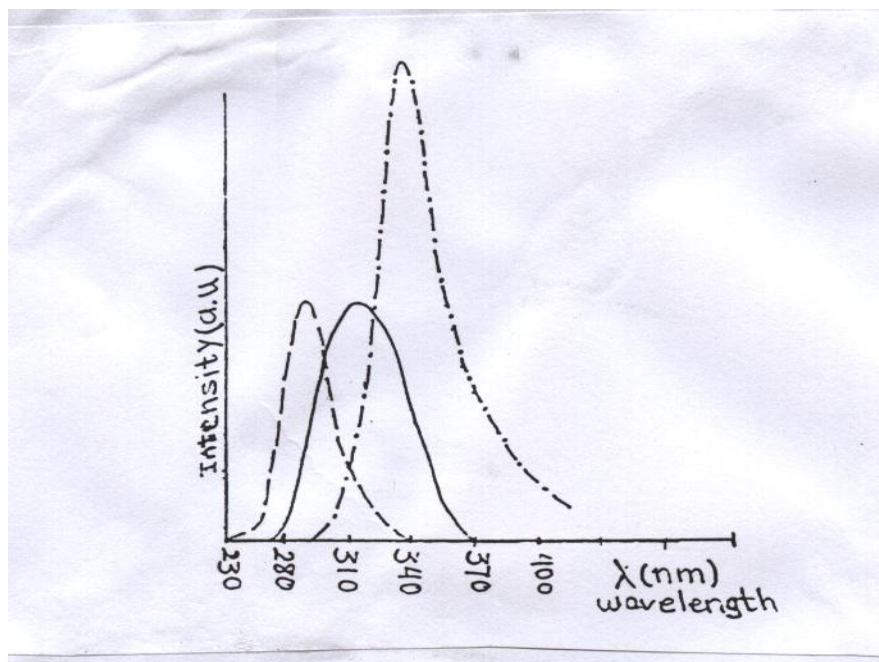


Fig.2. Excitation spectra of bis-oxadiazole compounds in toluene,
 ----- 4-Me; _____ 4-Et; -.-.-.- 4-Be

Table 2: Singlet excited state energy E_{S_1} (kJ/ mol)of the compounds in various solvents.

Compound	Toluene	Ethanol	DMSO
4-Me	364.82	345.84	373.94
4-Et	346.84	342.85	371.62
4-Ben	341.89	336.13	-----
8-Me	332.93	349.89	-----
8-Et	357.2	347.85	-----

It is interesting to note that increasing the chain length between the oxadiazole rings from $n=4$ to $n=8$ results in the opposite effect of the substituent. This may indicate the clear affect of the CH_2 chain on the energy of S_1 state in toluene solvent due to the possible orientation motion occur in the long chain compounds ($n=8$) which leads to many interactions such as intermolecular interactions (ie Van der walls) between CH_3 or C_2H_5 groups and the neighboring

sulphonyl part of the molecule. For the 8-Me compound, the E_{S_1} is lower than that of 8-Et compound (Figure-3).

The picture of the excitation spectra and S_1 energy of these compounds in ethanol solvent is different; (a) there are more than one peak for the compounds 4-Me and 4-Et and 4-Ben, with a low intensity peak at 280 nm. (b) Changing the CH_2 - chain length has a little effect on the absorption maximum of 4-Me and 4-Et

compounds compared to that seen in toluene solvent (see table-1-). Also this is clear in the E_{S_1} picture presented in Table-2-. In the case of DMSO solvent there is a red shift in the absorption peak in going from 4-Me to 4-Et compound as presented in Figure -4-.

From the data obtained in this work it is obvious to say that many effects other than solvent polarity may affect the position of the S_1 state of these compounds

(e.g., Orientation effect, Vander Waes interaction.).

Fluorescence processes

The fluorescence intensity of the compounds 4-Me,4-Et and 4-Ben in all solvents used increases in going in substitution by CH_3 to C_2H_5 to $CH_2C_6H_5$ groups at the ends as presented in Table-3- and shown in Figure-5-.

Table 3: Spectroscopic data of the fluorescence emission of the bis-Oxadiazole Compounds at short wavelength.

Compound	Toluene	Ethanol	DMSO
	λ_{emiss} nm (max)	λ_{emiss} nm (max)	λ_{emiss} nm (max)
4-Me	350	368	335
4-Et	370	360	340
4-Ben	371	374	-----
8-Me	420	360	-----
8-Et	385	364	-----

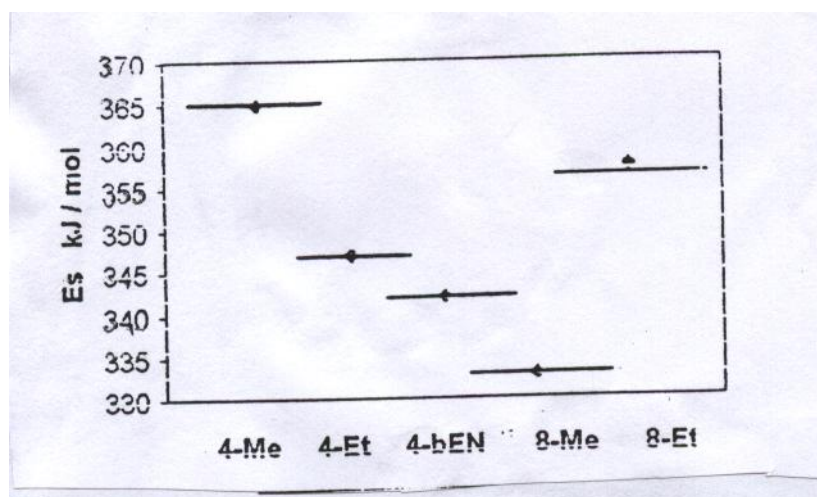


Fig.3. Energy diagram of S_1 state of the compounds in toluene.

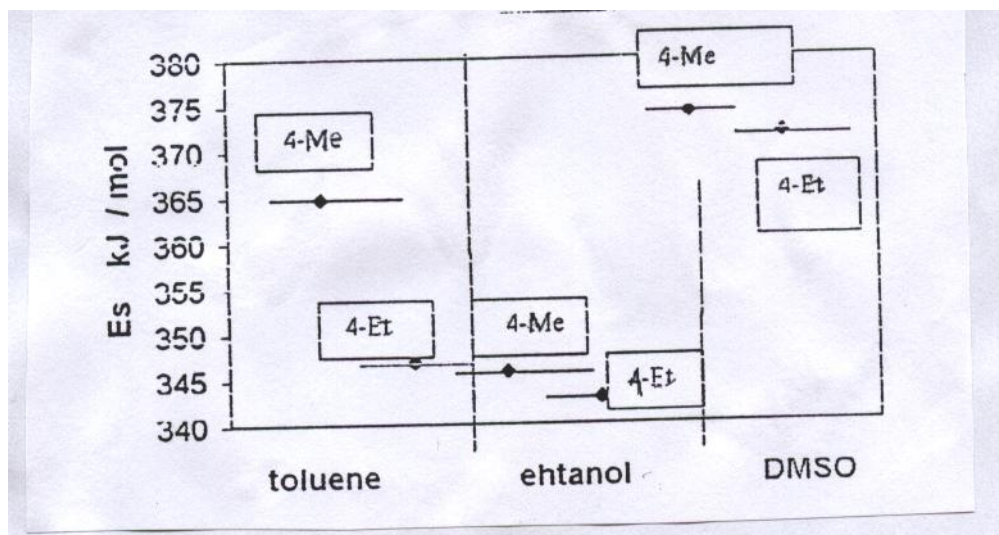


Fig.4. Energy diagram of S_1 state for 4-Me and 4-Et in different solvents.

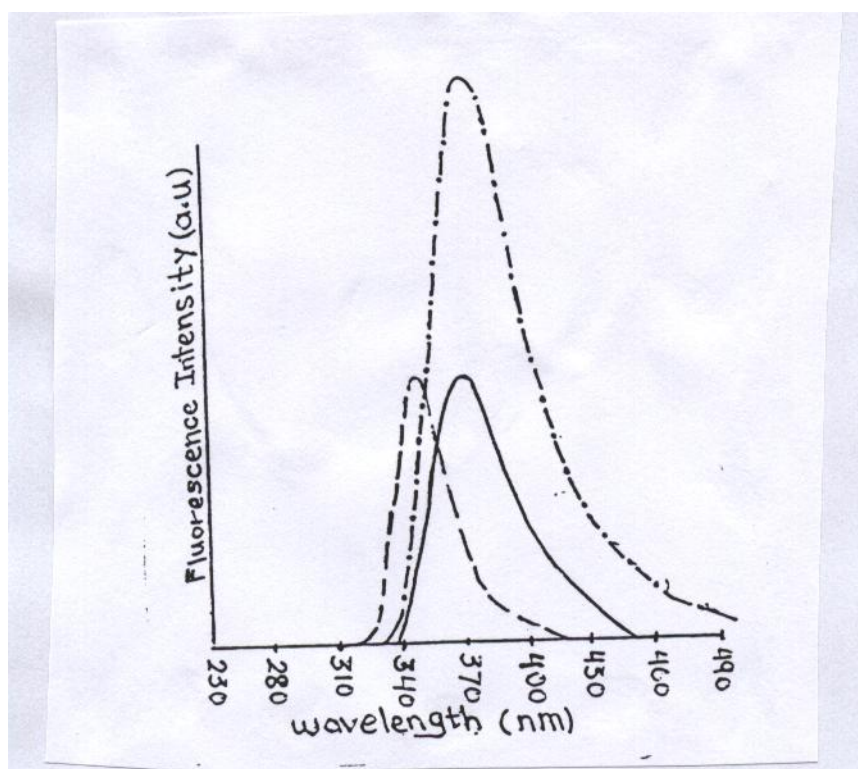


Fig.5-a. Fluorescence spectra of bis-oxadiazole compounds in toluene; ----- 4-Me, _____ 4-Et, -.-.-.-.- 4-Be .

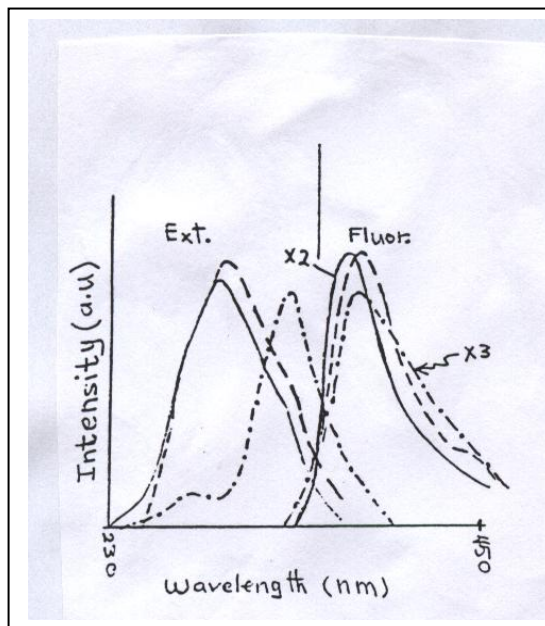


Fig.5-b. Excitation and fluorescence spectra in ethanol,
 ----- 4-Me, _____ 4-Et , -.-.-.- 4-Be.

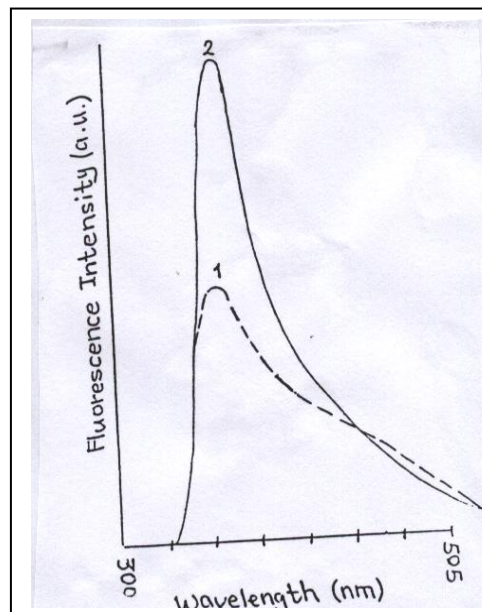


Fig.5-c. Fluorescence spectra of bis-oxadiazole compounds in DMSO solvent. ----- 4-Me , _____ 4-Et.

The fluorescence quantum yield represented as fluorescence intensity coincide with the values of $S_1 (n\pi^*)$ energy for the three compounds in the solvents used (see Figure-4- and Table-2-). Photo physically speaking, the difference in intensity between the three compounds may be due to the singlet-triplet energy gap, ΔE_{S_1-T} , in each solvent. The sequence of ΔE_{S_1-T} is for $4\text{-Me} < 4\text{-Et} < 4\text{-Ben}$ which affect on the rate of the nonradiative intersystem crossing S_1 T process , k_{ISC} for the three compounds. This leads to the conclusion that k_{ISC} , the intersystem crossing rate constant, for $4\text{-Me} > 4\text{-Et} > 4\text{-Ben}$. depending on the theory that the high k_{ISC} results from the low energy difference between the excited singlet and triplet states ΔE_{S_1-T} and this consequently results in a lower fluorescence intensity. The

position of the fluorescence maximum of the three compounds does not obey the sequence of solvent polarity or group substituent effects (see Figure-5-).

In the case of the compounds 8-Me and 8-Et, the fluorescence intensity in toluene is quite larger than that in ethanol solvent as shown in Figure-6- .Also, the fluorescence intensity of 8-Et compound is 10 times larger than that of 8-Me in toluene and ethanol solvents which might be due to the small energy difference between singlet and triplet states for 8-Et compound.

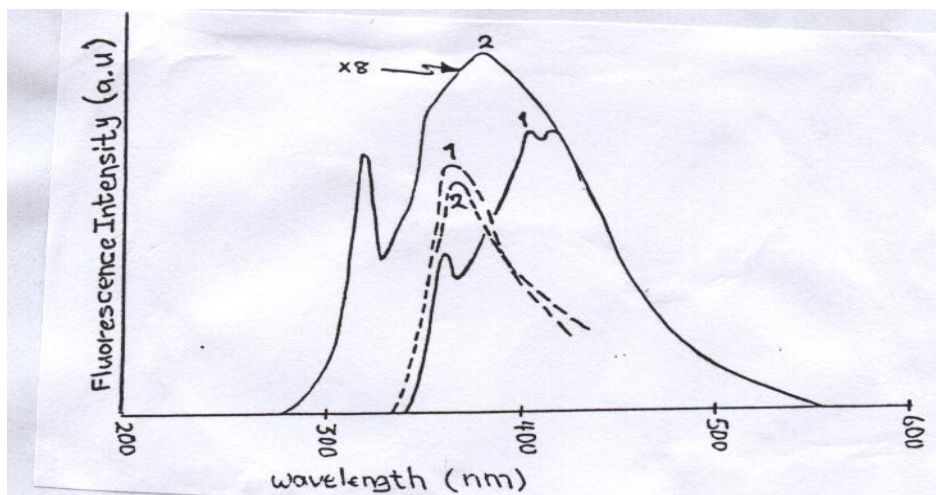
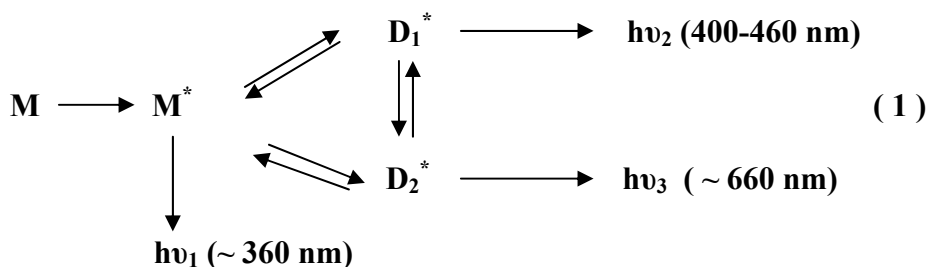


Fig.6. Fluorescence spectra of bis-oxadiazole compounds
1- 8-Me, 2- 8-Et ; _____ in toluene, ----- in ethanol solvent.

Long wavelength emission

The emission at wavelength longer than 500 nm is not observed for the compounds (4-Me, 4-Et and 4-Ben) when they dissolved in toluene. In ethanol these compounds possess a low intensity emission between 550-690 nm with a maximum peak around 662 nm as illustrated in Figure- 7-

This emission may be initiated from a low energy singlet state of an intermolecular excited complex D_2^* in the polar environment⁹. Furthermore, an intense and broad emission is observed around 400-460 nm which most probably is due to an excimer D_1^* fluorescence. The general reactions are shown in equation (1).



Fluorescence quenching

The fluorescence emission behavior of the compound 4-Et in ethanol is examined in the presence of two compounds: Benzophenone and benzonitrile:

a- Quenching by benzophenone

Benzophenone ($E_{S1} = 309.6 \text{ kJ/mol}$, $E_{T1} = 288.69 \text{ kJ/mol}$), with concentration of $\sim 10^{-4} \text{ M}$, is used

to quench 4-Et fluorescence when excited at 275 nm. From the quenched fluorescence spectra and Stern-Volmer plot one can notice the following:

- 1- The quenching of the 4-Et fluorescence peak at 360 nm is with a dynamic pattern (Figure. 8-a).
- 2- a new fluorescence emission peak at longer wavelength (420 nm)

The suggested mechanism propose the formation of a complex between like molecules, i.e. D_1^* , as in step 3. These complexes emit fluorescence (step- 4) or might undergo through a quenching process of energy transfer type (step-5) or through the ordinary quenching mechanism (step-6). The other proposition is the formation of another complex D_2^* between alike 4-Et molecules in the ground and

excited singlet states (step-7) that have an energy lower than that of D_1^* complex. This complex may deactivated by two processes, the first is the emission at 662 nm (step-8) and the other is the quenching of the excited complex due to the presence of benzophenone (Be) molecules (step-9) which observed as quenching of the 662 nm emission peak.

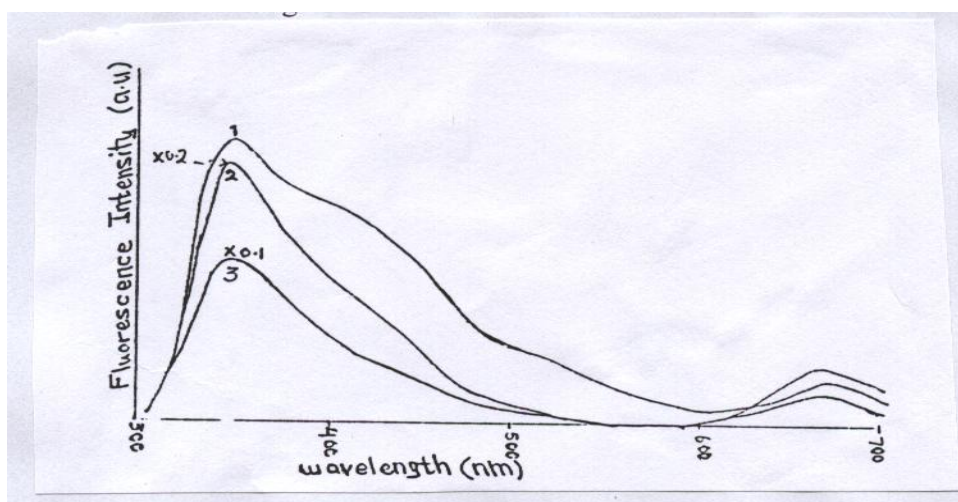


Fig.7. Short and long wavelength emission of some bis-oxadiazole compounds in ethanol solvent , 1, 4-Me ; 2, 4-Et ; 3, 4-Be

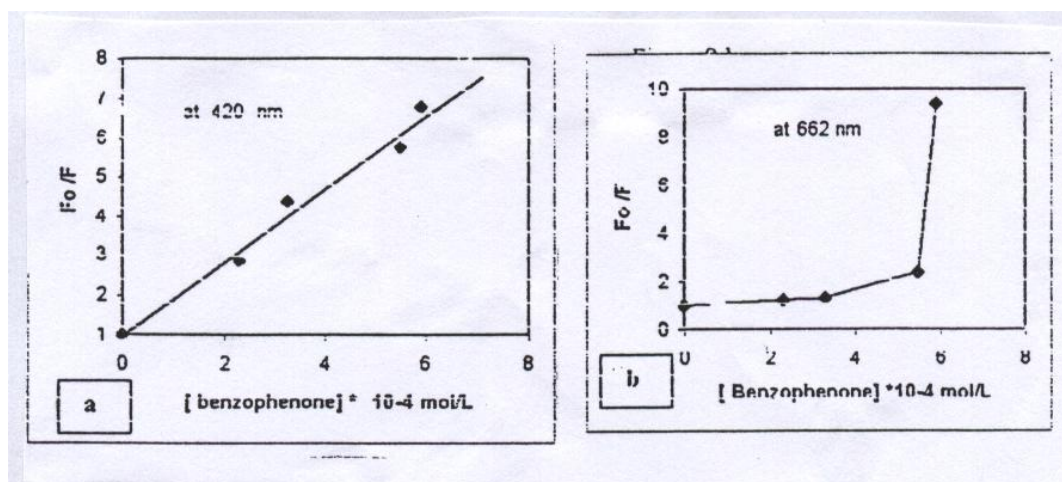


Fig.8. Stern-Volmer plot of 4-Et by benzophenone in ethanol , (a) at 360 nm , (b) at 662 nm.

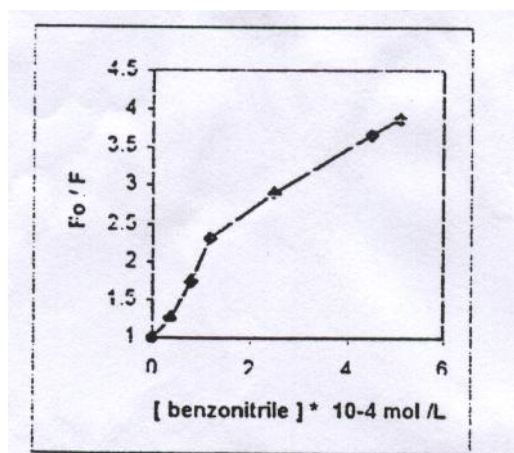


Fig.9. Stern-Volmer plot of 4-Et by benzonitrile in toluene.

Conclusion

Bis-(sulphonyl-oxadiazole) compounds possess an intense fluorescence. In ethanol 4-alkyl oxadiazoles gave emission at both short and long wavelengths. The position and intensity of the absorption and fluorescence spectra were structure and chain length dependence. The quenching mechanism of 4-Et fluorescence by benzophenone is thought to be a complex process and involve more than one type of quenching.

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References

- 1- Rai,L.and Singh,R.A.,Acta.Sci.B.N.,*Indian*, 1983, **9**, 15.
- 2- Morrin, M.and Mysinger, D., *Pharmazie*, 1983, **38(8)**, 56.
- 3- Mustafa, I.F., Mu, *tah J. of Res. And Studies*, 1997, **12(3)**, 153.
- 4- Mahmoud,M.J.,Mustafa,I.F.,Ali,M.A., *Ibn Al-Haitham J.for pure and*

Appl.Sci., 1999, **11(2)**, 82.

5- Omar, S.S.and Mustafa, I.F., *Basrah J.for Science*, 2000, **C-18(2)**, 205.

6- Omar,S.S. and Mustafa,I.F., *Iraqi J. of Chem.*, 2001, **27(4)**, 861.

7- Omar S.S., Unpublished results.

8- Mahmoud,M.J. Mustafa,I.F. , Ali,M.A., *Proceeding of the first science*

conference, Mwtah University, 1997, **1**, 191.

9- Strehmel, B., *Advanced Functional Molecules and Polymers*, 2001, **3**, chapter

7, 299, Edited by H.S.Nalwa, Overseas Publishers Association,N.V.