A New Theory upon the Fluorescence and Chemical Constitution of Organic Compounds

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(Received April 30, 1951)

Introduction

The relation between fluorescence and chemical constitution of organic compounds has been studied since old times[1-14], but we have not seen any satisfactory theories upon this subject to this day.

All of the hitherto published theories are rudimentary or limited in their scopes; therefore they do not explain satisfactorily the relation between fluorescence and chemical constitution of numerous organic compounds known at present.

We have synthesized many organic fluorescent substances and studied this problem deeply and widely; in consequence we have contrived a new universal theory.

We have applied to nearly one thousand organic fluorescent compounds our theory, and recognized that the theory supported itself very well in any instances.

Therefore, we should be like to publish our theory.

I. The Condition for the Emission of Fluorescence

As understood from the energy curve which indicates the energy state in a molecule of organic compounds, in order to fluoresce, organic compounds need to have such structure as is easily excited, is able to cause electron migration, and does not bring about the transition of non-radiation of excited energy.

The easier the electron mobility is, and the larger the intensity of absorption is, the greater the emissivity of fluorescence becomes. From this easiness of electron mobility, the following 1st and 2nd conditions arise, and such conditions also make intensity of absorption increase for the reason explained later.[15]

1st condition.

The molecule needs to have a structure of conjugation system.

Example: naphthalene, anthracene, phenanthrene, and diphenyloctatetraene.

But to make the emissivity of fluorescence more effective, and to obtaine substances of the strong emissivity of fluorescence, it would be necessary to combine the first condition with the following second.

2nd condition.

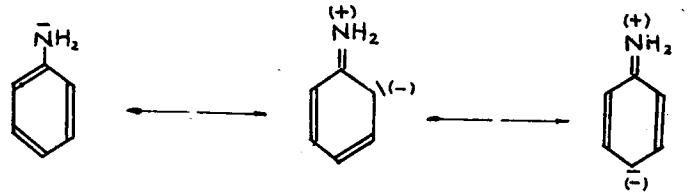
As a result of resonance (Mesomerie) in conjugation system containing certain substituents such as amino- or cyano-group, the electron density of the double bond atom does change.

Then, we wish to deal with the following:

+M substituents mean those which have the effect of making+charge arise on the double bond atom (i. e., those which make the electron density of the atom decrease), and −M substituents mean those which have the effect of making −charge arise on the double bond atom (i. e., those which make the electron density of the atom increase).

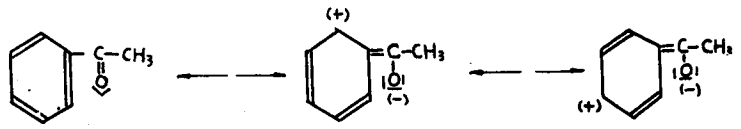
Example:

1) Aniline resonates followingly:



In o- or p-position, electron density is large. Therefore, amino group is a −M substituent.

2) Acetophenone resonates followingly:



In o- or p-position, electron density is small. Therefore, carbonyl group is a +M substituent.

R. Robinson[16] considered that as result of resonance, amino-group can carry the unshare electron to double bond atom of conjugation system; namely, it has the action of the electron donor.

In Table I, −M and +M substituents are shown.

An example in which emissivity of fluorescence of organic compounds containing, for instance, −M subtituent becomes more effective than in the case of conjugation system only is as follows.

Table I

−M substituents	+M substituents
$-\overset{(-)}{C}R_2 > -\overset{(-)}{N}R_2 > -\overset{(-)}{O}$	$-X=\overset{(+)}{N}R_2 > -X=NR$
$-\overset{(-)}{N}R > -\overset{(-)}{N}R_2$	$-X=O > -X=S$
$-\overset{(-)}{O} > -OR > -\overset{(+)}{O}R_2$ (S) (S) (S)	$-X=O > -X=NR > -X=CR_2$
$-NR_2 > -OR > -F$	$-X\equiv N$
$-OR > -SR$	X; C or N

Benzene fluoresces in ultraviolet range (268–310 mμ), but pyrrole does not fluoresce. However, naphthalene and indole fluoresce in ultraviolet range, but the intensity of fluorescence of indole is greater than that of naphthalene.

Now, we will describe the 2nd condition.

If +M or −M substituent exists in the following condition, the emissivity of fluorescence may become greater than in the case of conjugation system only.

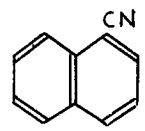
I) The case in which there is either one +M substituent or one −M substituent. In this case, it is necessary that the substituent is at the end of conjugation system. In the case of ring conjugation system, it may exist anywhere.

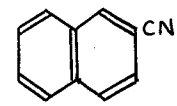
Example:

a) The case of existence of +M substituent.

Cyanobenzene

α- & β-Cyanonaphthalene





All have the intense fluorescence in ultraviolet range.

b) The case of existence of −M substituent.

This example is shown in Table II.

Table II

Substance	−M substituent	Fluorescence Band (mμ)	Intensity of Fluorescence
benzene		268—310	10
aniline	$-NH_2$	213—407	20
phenol	−OH	286—364	18
anisole	$-OCH_3$	231—245	20

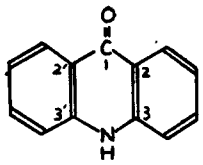
The Table II shows how −M substituents are effective on the emissivity of fluorescence.

II) The case of co-existence of +M− and −M substituents.

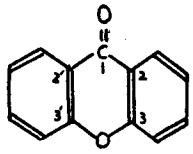
It is necessary that −M substituents exist in the atom of small electron density against +M substituent, and +M substituents exist in the atom of large electron density against −M substituent.

Example:

Acridone



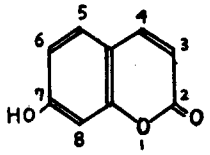
Xanthone



When we fix our eyes on the carbonyl group which is a +M substituent, the electron density is large in 2- or 2′-position and is small at 3- or 3′-position. −NH− or −O− which is a −M substituent combines with carbon atoms of 3- and 3′-position. Therefore, according to the present authors' theory, these compounds will fluoresce. The fact is also in accordance with the present authors' theory that these compounds fluoresce blue-violet in the benzene solution.

When we also fix our eyes on the −NH− or −O− instsead of carbonyl group, the result is the same.

Umbelliferon (7-Hydroxycoumarine)



It is considered that the electron density is large at 3-, 6-, 8- and 10-positions, and small at 2-, 4-, 5-, 7- and 9-positions, when we fix our eyes on the carbonyl group (2-position).

Therefore, it is very favourable to the emissivity of fluorescence that −O−, −M substituent, combines with the carbon atoms of 2- and 9-position, and hydroxyl group (−OH), −M substituent, combines with the carbon atom of 7-position.

The aqueous solution of umbelliferon has blue fluorescence. The intensity of fluorescence becomes especially great because of its alkali salt formation. This fact will be due to that −M effect of $-\overset{(-)}{O}$ is greater than that of hydroxyl group.

Next, 6- or 8-hydroxycoumarine, in which hydroxyl group combines with the carbon atom of high electron density, does not fluoresce. The present authors' theory explains well this fact. And, both 3, 4-dihydroumbelliferon, and 5, 6, 7-

trihydroxycoumarine also do not fluoresce. Because, in the former, since the addition of hydrogene to 3- and 4-positions cuts off the conjugation system in umbelliferon, the effect of +M substituent disappears, and in the latter, the planar configulation which is the condition of complete formation of resonance is difficult for the reason of the existence of three −M substituents in the benzene ring.

III) The case in which substituents of the same effect as the above two exist. Following two cases take place:

(i) The case of combined existence of these substituents with the same atom. This case is particular in Case I. Fluorescence becomes more intense than in Case I due to the co-action of substituents of the same effect.

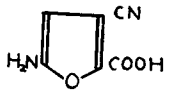
Example:

(a) Case of +M substituents.

+M substituent, such as $-COCH_3$ and $-COOH$, being combined with p-position of umbelliferon, fluorescence becomes more intense than in the case of umbelliferon.

(b) Case of −M substituents.

5-Amino-3-cyanofurancarboxylic acid



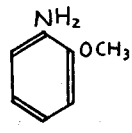
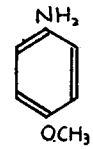
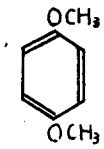
−M substituent; $-\overset{\bullet}{O}-$ and $-NH_2$

This compound fluoresces blue-violet in alcoholic solution.

(ii) The case of combined existence of these substituents with different atoms. It is necessary that −M substituents combine with the atom of large electron density against another −M substituent. But it is generally not favourable to emissivity of fluorescence that +M substituents having the electron with-drawing action exist with the above two in one molecule. However, in the case of two +M substituents existing, if one +M substituent exists combined with the atom of small electron density against another +M substituent in the middle part of linear conjugation system, the compound fluoresces.

Example:

(a) Case of −M substituents.

	o-Anisidine	p-Anisidine	Hydroquinone dimethylether
			
Fluorescence Band (mμ)	313-429	339-423	303-400

These compounds are in accordance with the present authors' theory, and all of them fluoresce. But resorcinol dimethylether which is not included in our theory does not fluoresce.

Following carbazole derivatives also fluoresce:

1- or 3-aminocarbazol, 3, 6-diaminocarbazole.

(b) Case of +M substituents.

For example, terephthalonitrile and o-carboxybenzonitrile do not have fluorescence. It is considered that the electron mobility is disturbed, since electron is sucked in by two +M substituents at the both ends of conjugation system.

But α, α'-dicyanostilbene, which has such structure as in accordance with the present authors' theory, fluoresce more intensely than stilbene.

As above mentioned, the 1st and 2nd conditions mean that the easier the electron mobility owing to resonance is, the greater the emissivity of fluorescence becomes. And also, the greater the intensity of absorption is, the more the emissivity of fluorescence increases.

Whereas, the intensity of absorption (or the extinction coefficient) is in close relation with ionic structure owing to resonance.[15] Therefore, 1st and 2nd conditions are important not only from the point of electron mobility, but from the point of increasing the intensity of absorption, and both after all make conditions of emissivity of fluorescence. But it comes into question here that the emittance of fluorescent light is generally so difficult as to cause the color deepened. And all −M substituents belonging to authochrome, therefore, the introducing of many −M substituents into one molecule is not favourable to the emissivity of fluorescence, since it enhances the color-deeping effect and further destroys the planar configulation which is the condition of the complete formaticn of resonance.

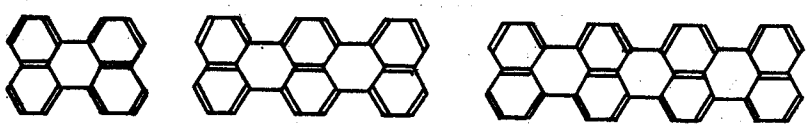
Naturally, there are also visible and invisible ranges in the fluorescence, like in common light, and there are various colors in the visible range. These various colors of fluorescence will be obtained by means of removing the absorption band to longer wave length, e. g., introducing authochromes suitablly or making the molecule large.

We will set forth actual examples in the following.

II. The case in which the compounds have the conjugation system only

i) Condensed cyclic compounds.

Benzene, naphthalene, anthracene, phenanthrene, naphthacene, 1,2-benzanthracene, triphenylene, crysene, pyrene, fluorene, dinaphthophenanthrene, perylene[17] (I), terrylene[17] (II), quaterrylene[17] (III),

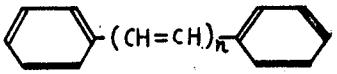


(I) (II) (III)

9, 9′, 10, 10′-tetraphenyl-1, 1′-bianthracene[18], 1, 2-(or 3, 4)-benzopyrene, 2, 3, 1′, 8′-binaphthylene[19],. 1, 2-benzopentacene[20], 1, 2, 3, 4-dibenzopentacene[20], 1, 2, 3, 4-dibenzonaphthacene[20], etc.

ii) Polycyclic compounds.

Diphenylpolimethine compounds:



n=0-3 : ultraviolet fluorescence.

n=4 : i.e., 1, 8-diphenyloctatetraene has visible fluorescence in crystalline state and in solution.

Following compounds all fluoresce:

tetraphenyl-p-xylene, as-phenyl-o-tolyl-p-quinodimethane, p, p′-distyryl benzene, p, p′-distyryl stilbene-o, o′-disulfonic acid[21], etc.

iii) Heterocyclic compounds.

In the strict sense of the word, there are no compounds having the conjugation system only in heterocyclic compounds. These compounds all contain +M or −M substituents. But, in compounds possesing −N= in the ring member, +M substituent, −C=N− has scarcely good influence on the emissivity of fluorescence.

On the contorary, in xanthone, xanthene, carbazole, and indole etc., the emissivity of fluorescence is effected by +M substituent (>C=O) or −M substituent (−NH− or −O−).

So they are besides the question.

Pyridine corresponding to benzene is not fluorescent, and quinoline and isoquinoline, both corresponding to naphthalene, are less fluorescenf than naphthalene.

	Fluorescence Band (mμ)	Intensity of Fluoreucence
Naphthalene	312-377	4
Quinoline	384-488	3
Isoquinoline	384-476	1

In acridine, we can observe violet fluorescence in alcoholic solution. Its chloride becomes more fluorescent, because +M effect of $-C=\overset{(+)}{N}-$ is larger than

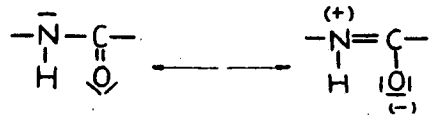
that of $-C=N-$. Following compounds also fluoresce:

methyl derivatives of benzacridine[22], (benzo-1′, 2′: 5, 6)-(pyridino-3″, 2″: 1, 2)-acridine, (benzo-1′, 2′: 1, 2)-(pyridino-2″, 3″: 7, 8)-acridine, quinolino-2′, 3′: 1, 2-acridine, phenazine, naphtho-2′, 3′: 1, 2-phenazine, 1, 2: 6, 7-dibenzophenazine, 1, 2: 7, 8-dibenzophenazine, 1, 2: 5, 6-dibenzophenazine, dianthrazine, tetrabenzo-phenazine, 3, 4: 5, 6-dibenzophenazine, etc.

As understood from the above example, condensed cyclic compounds are generally more effective than polycyclic compounds to the emissivity of fluorescence. And, having $-N=$ instead of $-CH=$ as a ring member makes the emissivity of fluorescence decrease. This may be due to that the electron mobility in the nucleus decreases because of the strong electron sucking action of $-N=$.

iv) Compounds containing amido group.

Amido group resonates as follows:



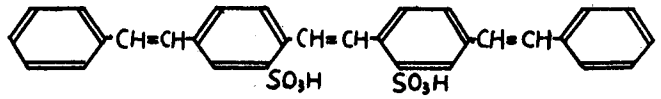
It is considered that amido group is useful for partial connection of conjugation system; therefore, compounds having amido group between the conjugation systems will fluoresce.

It is supported by the spectroscopic experiment of v. Auwers[23] that amido group resonates as above.

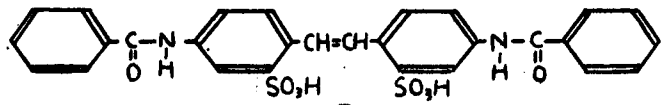
Example:

Dibenzoylbenzidine, diacetylbenzidine, 4, 4′-diacetylaminostilbene-2, 2′-disulfonic acid, 4, 4′-bis (4-acetylaminobenzoylamino)-stilbene-2, 2′-disulfonic acid, etc.

However, amido group is not of course the double bond, so these compounds have not themselves the nature of perfect conjugation. Therefore, these are less fluorescent than the corresponding compounds having the conjugation system only, e. g.,



(I)



(II)

(I) is more fluorescent than (II).

III. The case in which +M− and −M substituents combine with the atom of the conjugation system.

This case is most general in organic fluorescent substances. Numerous examples are known.

i) Benzene derivatives.

Compounds combining −M substituents with benzene are shown in Table III. In the case of the two −M substituents existing, p-isomer is generally is more intense than o-isomer in the emissivity of fluorescence.

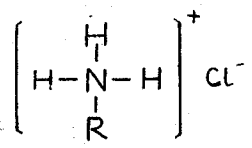
These fact will be due to the steric hindrance.

Table II

Substance	−M substituent	Fluorescence		Absorption band (mμ)
		Band (mμ)	Intensity	
bonzene		268—310	10	236—272
anisole	OCH_3	281—345	20	238—282
phenol	OH	286—364	18	238—288
aniline	NH_2	313—407	20	260—305
dimethylaniline	$N(CH_3)_2$	325—394	10	271—310
o-anisidine	NH_2, OCH_3	313—429	17	262—305
p-anisidine	NH_2, OCH_3	339—423	13	267—314

In the case of nitro group existing, which has the nature of the strong electron sucking, if nitro group exists with the atom of small electron density in aniline, this compound (m-nitroaniline) fluoresces. On the contorory, if nitro group exists with the atom of large electron density in aniline, these compounds (o- and p-nitroaniline) do not fluoresce. It is the same in naphthylamine etc..

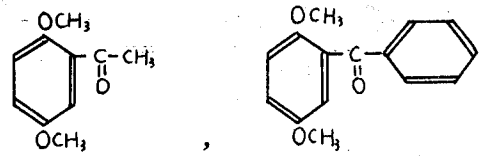
And, anilinehydrochloride and naphthylaminenhydrochloride do not fluoresce. This is attributed to that −M effect of amino group disappears with the salt formation.



R: phenyl, naphthyl.

These facts are will explained by the present authors' theory.

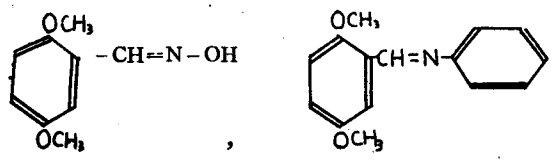
In the following two compounds,



the former is fluorescent, but the latter is scarcely so, for the reason that phenyl group has the nature of electron pool, or is electrically negative.

Therefore, by introducing hydroxyl group instead of phenyl group, the compound (i. e., 2, 5-dimethoxybenzoic acid) is made fluorescent. That is, +M effect of carbonyl group decreases in the case of phenyl group, but does not decreases in the case of electropositive group such as $-CH_3$ or $-OH$.

Following compounds also belong to such an instance:



The former fluoresces in violet, but the latter does not fluoresce in alcohclic solution.

Further, following compounds are given for benzene derivatves:

hydroxycompounds of benzene[24], hydroquinonedisulfonic acid, hydroquinonetetracarboxylic anhydride, 2, 5-dimethoxybenzalmalonicdinitrile, 2, 5-dimethoxy-α-cyanocinnamic ester, 2, 5-dimethoxybenzal indandion, 2, 5-dimethoxy-α-benzoylcinnamic nitrile, o-hydroxybenzoic acid, anthranilic acid, o-aminocinnamic acid, aminoterephthalic acid, 2, 5-diaminoterephthalic acid, 3-aminophthalic anhydride. and so on.

ii) Polycyclic and condensed cyclic compounds.

compounds belonging to ii) are as follows:

benzidine and its various derivaties, 4, 4′-diamino-(or dihydroxy) stilbene and its derivatives, p-dimethylaminostilbene, 4-methoxy-4′-cyano-α, α'-diethylstilbene[25], 4, 4′-diaminochalkon,[26] α-(or β-) naphthylamine, α-(or β-) naphthole, naphthionic acid, R-acid, α-(or β-) naphthylurea, α-(or β-) naphthylthiourea, 4, 4′-diureidostilbene-2, 2′-disulfonic acid[27], naphthalene dicarboxlic anhydride[28], 1, 5-naphthalene-bis (azo-2-naphthylamine)[29], 4-amino-1, 8-naphthalimide derivatives[30], 3-aminopyrene-5, 8, 10-trisulfonic acid, 9-hydroxy(or amino-) anthracene, 3, 4, 9, 10-tetraphenyl-1-hydroxyanthracene[31], and anthrahydroquinone.

iii) Heterocyclic compounds.

Compounds belonging to iii) are very abundant. So only main compounds are given. 5-amino-3-cyanofurancarboxylic ester[32], chloraminomaleic imide[32], methylaminocitraconic methylimide[33], and

Thiazole derivatives such as:

2-mercapto-4-methyl-5-acetoxyethyl thiazol[34], Na-2-mercapto-4-methylthiazolecarbonate (5)[34], 1-(4-methylthiazolyl (2)-amino)-naphthalene-4-sulfonic

acid,[35] 4-(4-ethoxyphenyl) thiazole[36], pyridylthiazole derivatives[37], and bithiazoles[38].

Oxazole derivatives[39] such as:

2, 5-diphenyloxazole, 2-phenyl-5-veratryloxazole, (but, 5-phenyl-2-benzyloxazole, 2-benzyl-5-veratryloxazole are not fluorescent, because of destruction of conjugation between phenyl group and oxazole nucleus.) 5-phenyl-2-styryloxazole, 5-phenyl-2-(p-anisyl)-oxazole, 2-styryl-5-(p-anisyl) oxazole, 5-phenyl-2-(p-anisyl) -oxazole, 5-phenyl-2-α-naphthyloxazole, 5-phenyl-2-(p-hydroxyphenyl) oxazole, and 5-hydroxy-4-methyl-2-phenyloxazole.

Pydidine derivatives such as:

α-aminonicotinic acid, 4, 5-diaminopyridine derivatives[40], dihydrokollidine dicarboxylic ester[23], 2-(ethylmercapto)-4-hydroxy-5, 6-trimethylene pyrimidine[40], and N-methyl-α-pyridone derivatives[11].

Benzoxazole derivatives[6] such as:

2-o-(or m- or p-) tolyl-6-hydroxybenzoxazole, 2-phenyl-6-hydroxy-5-toluoxazole (but, 2-methyl-6-hydroxy-5-toluoxazole does not fluoresce, because conjugation grows shorter), 5-methyl-2-(3-aminophenyl) benzoxazole, and 5-methyl-2-(4 -aminophenyl) benzoxazole.

Flavone derivatives[41] such as:

5, 6-dimethoxy-3-hydroxyflavone, 3, 5, 6, -trihydroxyflavone, 3, 5, 6-trimethoxyflavone, 4′, 5, 6-trimethoxy-3-hydroxyflavone, 3, 4′, 5, 6-tetramethoxyflavone (above compounds are less fluorescent than the compound introducing $-OH$ to 7- position instead of 3-position. This is a matter of course from the present authors' theory.), 6, 7, 8-trimethoxyflavone, 4′, 6, 7, 8-tetra-methoxyflavone (but 3, 3′, 4′, 7-tetramethoxyflavone has only feeble fluorescence, since the positions and a large number of $-M$ substituents are not too favourable.), and 4′ -amino- 7, 8-bonzoflavone.

Coumarine derivatives[12], [42] such as:

umbelliferon, 7-hydroxy-3-acetylcoumarine, 7-hydroxy-3-cyanocoumarine, 7-hydroxy-3-cyanocoumarine, 7-hydroxy-8-methyl-3-acetylcoumarine, 7-hydroxy-8-methyl -3-coumarinecarboxylic ester, 7-hydroxy-3-coumarine carboxylic acid (these compounds introducing $-M$ substituent to 3-position of umbelliferon fluoresce more than umbelliferon, but this superiority disappeare with screening of $+M$ effect, e. g., introcucing of $-CH_2-$ between the coumarine nucleus and $-COOH$. Thus, 7-hydroxy-3-coumarine acetic acid does not fluoresce more than umbelliferon. When $+M$ substituent also exist in 4-position instead of 3-position of umbelliferon, no superiority in the emissivity of fluorescence is recognized. These facts are explained by the present authors' theory.), 5-methoxycoumarine (but, 6- or 8-hydro-

xycoumarine does not fluoresce.), 7-amino-5-methylcoumarine, and 5, 6-benzocoumarine-3-carboxylic acid.

Quinoline derivatives such as:
3-aminoquinoline, 6-methoxy-4-quinolineacrylic acid[43], 2,8-dimethyl-4-hydroxy-6, 7-benzoquinoline[44], 2-hydroxy-4, 9, 10-trimethyl-1, 5-anthrazoline, 2-(2-dibenzofuryl)-quinoline[45], 4-hydroxy-2-methyl-6, 7-benzoquinoline[46], 3, 4-diamino-6, 7-benzoquinoline, 4-hydroxy-6, 7-benzoquinoline, 4-chlor-8-aminoquinaldine, and 5-carboxy-7-aminoquinaldine.

In heterocyclic compounds, described in II-iii), such as quinoline and acridine, we need not to consider +M effect of $-C=N-$ on the emiesivity of fluorescence, and may treat them as compounds which have the conjugation system only, and fluoresce less than the corresponding hydrocarbones.

However, when one $-M$ substituent exists in these compounds following two cases take place:

a) The case in which electron (or charge) migration takes place between $-M$ substituent and $-C=N-$.

b) The case besides a).

In a), we may treat such a compound as nucleus having the conjugation system only and being more fluorescent than the corresponding hydrocarbone, and in b) as the basis of original heterocyclic compound.

Thus, for example, the emissivity of fluorescence in quinoline is as follows: quinoline substituted 2-(4-, 5- or 7-) position by $-M$ substituent $>$ naphthalene $>$ quinoline.

Acridine derivatives[47] such as:
2-aminoacridine, its 6-(or 8-) chlorderivative, 9-methyl-2-dimethylaminoacridine, 3-aminoacridine, its 6-(or 8-) chlorderivative (its nitrocompound does not fluoresce in day-light, and has feeble fluorescence in ultra-violet ray.), 7-amino-2, 3-(or 3, 4-) benzacridine, 9-aminoacridine, and its following derivatives: 4-(or 2-) phenyl-, 1-(or 2-, 3-) methoxy-, 1-(or 2-, 3-, 4-) chlor-, 2-cyano-, 2-(or 4-) carboxy-, mono-(or di-) acetyl derivative, 9-succinimidoacridine, 9-amino-2, 3-(or 3, 4-) benzacridine, 3, 6-diamino-1, 8-dimethylacridine, 3, 6-diamino-2, 7-di- ethoxyacridine, 3, 6-diamino-2, 7-dichloracridine, 3, 6-bis(methylamino)-2, 7-dimethylacridine, 3-amino-6-ethylamino-2-methylacridine, 3-amino-5, 6-benzacridine, 7-aminoacridine, 3-hydroxy-9-acridinecarboxylic acid, 9-chlor-7-amino-1, 2, 3, 4-tetrahydroacridine, and 9-amino-5, 6, 7, 8-tetrahydro-2, 3-benzacridine.

Acridone, and its following derivatives:
methyl-, hydroxy-, methoxy-[48], and 3, 4-dihydro-1, 2-benz derivative.[49]

Carbazone derivatives[50] such as:
2-aminocarbazone, and 2, 4-(or 2, 5-) diaminocarbazone.
Aminopheno-naphthazoxon, benzcarboline derivatives[51], dinaphthylenedioxide, and its derivatives[52], pterin or thiopteridine derivatives[53], 6-amino-9-phenylfluorone, 3, 6-bis(dimethylamino)-xanthone, fluoridine, dehydrothio-p-toluidine, tricresylphosphate.

Dyestuffs[54] such as:
acronoll yellow TS, primuline yellow, chlorazol pink Y, acridine orange L, brilliant green, fuchsine, methyl-violet, safranine A, magdala red, chlorazol violet R, chlorazol blue RW, oil red TV, congo red, eosin, uranine. rhodamine, auramine, violanthrone, isoviolanthrone, and indanthrene gold orange.

Optical bleaching agents[55] (brightner) such as:
β-methylumbelliferon, 5, 6-(2-sulfobenzo) -4-methylumbelliferon, p, p′-bis (p-acetylaminobenzoylamino)-stilbene-o, o′-disulfonic acid, Blankophor B, Blankophor R, Uvitex RS, Uvitex WS, 2-styrylbenzimidazole, 1, 5-bis(5-sulfo-2-benzimidazolyl) furan, sulfonated 4, 5-diphenylimidazolone (Blankphor WT), and so on.

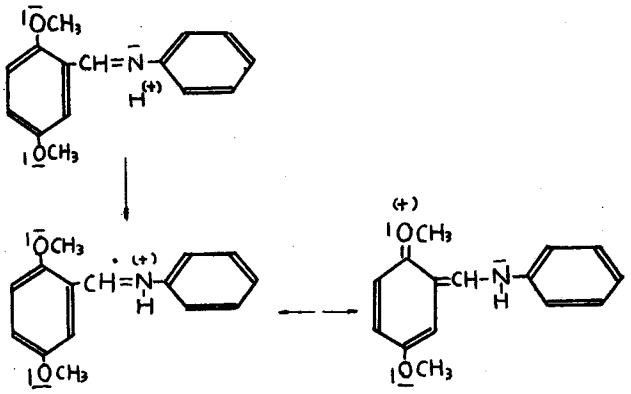
Sensitising dyes such as:
cyanine, isocyanine, orthochrom T, pinachrom, pinarerdol, pinacyanol, pinachrom blue, dicyanine, dicyanine A, kryptcyanine, thiocyanine, thiocarbocyanine, and neocyanine, etc.,

Further, we observe a large number of organic fluorescent compounds besides the above-listed fluoresce, but our theory will cover them all.

Conclusion

The present authors' theory upon the fluorescnece and chemical constitution of organic compounds has been expounded with the presentation of many examples, and each example has supports it well.

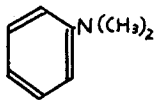
And, fluorescence due to "Halochromie" is also explained by our theory, For example, 2, 5-dimethoxybenzalaniline does not fluoresce in organic solvent, but fluoresces green in concentrated sulfuric acid. This will be due to −M effect of new produced iminogroup as follows:



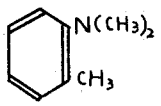
As regards the influence of substituents other than −M− and +M substituents, the inducing of nitro group to fluorescent compounds makes fluorescence decrease or disappear. Since nitro group has the strong electron sucking action, electron mobility in conjugation system decreases. Its effect is particular strong, when nitro group combines with the atom of the large electron density.

Methyl group has the effect of hyperconjugation, and is considered to be a kind of −M substituent. Therefore, the inducing of methyl group often makes the emissivity of fluorescence more intense as in the following example:

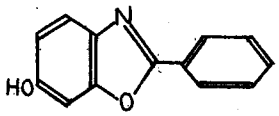
Dimethylaniline



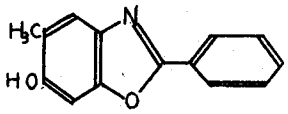
Dimethyl-o-toluidine



2-Phenyl-6-hydroxy-benzoxazole



its 4-methylderivative



As influence of other substituents has already been studied, we would omit its description.

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