PART V

Studies in the absorption spectra of acetoacet arylamides, hydroxyquinolines and their methylene bis-derivatives .

PART V

Theoretical

The absorption of light energy by an organic molecule causes a transition of the molecule from its ground state to an electronically excited state (ionic). The difference in energy of these states determines the frequency of the light absorbed. This is stated mathematically by the relation, $(E_1-E_0) = h\nu$, where E_0 is the initial energy of the molecule, E_1 is the energy of the molecule in its excited state, 'h', is the Planck's constant, and 'ν' is the frequency of the light absorbed. The smaller the difference in energy between the states, smaller the frequency or longer the wave-length of the light absorbed.

A number of factors may influence the energy values of the initial and final states, thus controlling the energy difference between the two states, and hence the wave-length of absorption. Resonance is important in considering the stabilization of both the ground state and the excited state. Structures involving a separation of charge contribute chiefly to the excited state and hence tend to resonance-stabilize the excited state more than they do the ground state. As the number of double bonds, in a conjugated system increases, the number of ground state structures does not increase as much as possible number of excited states and absorption shifts to progressively longer wave-length. Substituents alone do not produce absorption at wave-lengths, longer than 2000 A°, but they do alter the absorption of chromophoric groups (auxochromes). Usually, the bathochromic shifts (towards longer wave-length) are produced due to the interaction between the electrons of the chromophoric groups and those of the substituents.

There are many effects which influence the development of the absorption spectrum. These effects are : (a) effect of position of substituents (b) effect of saturated substituents (c) effect of unsaturated substituents (d) effect of steric hindrance (e) effect of fine structure and (f) effect of insulation. Now, in the insulation effect, if two or more chromophores or auxochromes exist in the same molecule but are separated from each other by insulating groups, there can be no effective interaction between them, and their spectral behaviour will be the same as if they were in separate molecules. A simple example is provided by 1,1-diphenylethane in which the two benzene rings are separated by a $-CH<$ group ; the spectrum resembles that of two molecules of toluene and not that of diphenyl. The spectra of the polynuclear compounds, containing such substituents as $-CH_2OH$, $-(CH_2)_nOH$, $-CH_2NH_2$ and $-CH_2-C_6H_5$, are essentially the same as the spectra of simple alkyl derivatives, because the chromophoric and the auxochromic groups are separated from the aromatic system by one or more methylene groups. (Friedel and Orchin, " Ultra Violet Spectra of Aromatic Compounds ", John Wiley and Sons., New York, 1951).

Changes in absorption spectra produced by constitutional changes in a molecule may involve a shift in the frequency or a change in the intensity of absorption or both. These effects are usually defined by certain terms.

A bathochromic effect is a shift of the absorption band towards lower frequencies. The opposite effect, representing a lightening of colour or a shift of the absorption band towards higher frequencies, is described as hypsochromic. A hyperchromic effect is an increase in the intensity of absorption, i.e. in the extinction coefficient of an absorption band, and the opposite effect is hypochromic. Now, when two or more chromophoric systems are present in a molecule, the effect is roughly additive if the systems are separated by two or more single bonds, i.e. by saturated groups such as $-CH_2-$ and $-CH_2-CH_2-$, which break the conjugation and act as insulators between the two electronic oscillators (Venkataraman, " The Chemistry of Synthetic Dyes ", Vol. I Academic Press Inc., New York, 1952, 312 and 358).

Mme. Ramart, Naik and Trivedi (Bull. Soc. Chim., 1934, 1, 525) studied the relationship between chemical activity and absorption in the ultraviolet of malon diarylamides. This type of work was extended by Ramart, Naik and Mehta (J. Ind. Chem. Soc., 1938, 15, 421) to the dichloro derivatives of malon diarylamides. Naik, Trivedi and Mankad (J. Ind. Chem. Soc., 1943, 20, 389) studied the ultraviolet absorption spectra of the amides of acetoacetic acid. It has been pointed out that the presence and the position of the methyl groups in the nucleus of the molecule with regard to -NH- grouping brings about a batho-chromic change in the curves. It is also of interest to note that the characteristic bands are observed, due to the presence of simple ketonic form, which is ascribed to the ketonic structure of the amide persisting in aqueous solution ; whereas the presence of enolic structure persists in the alcoholic solution. Further, Naik et al. (loc.cit.) have observed that the absorption curves of acetoacet-1:3:4-xylidide closely resembled that of acetoacet-o-toluidide, due to the similarity of structures of these two substances. The difference in the degree of absorption is due to the presence of $-CH_3$ group in the para position to -NH- group. Moreover, in the curves of acetoacet-α-naphthylamide and acetoacet-β-naphthylamide, the bands are characteristics of the naphthyl residue, viz., the disposition of the maximum between 2800-2400 A°. The distinct difference between the curves of α-naphthylamide and β-naphthylamide must be attributed to the structures of their amine residues.

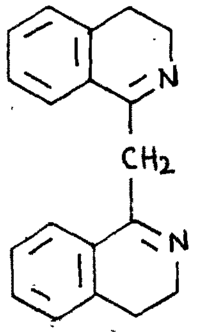
A study of the ultra-violet absorption spectra, in the light of restricted rotation and resonance of biphenyl compounds was made by O'shaughnessy and Rodebush (J.Amer.Chem.Soc., 1940,62,2906). They studied the effect of position of the substituents in the biphenyl molecule, which was previously observed by Pickett, Walter and France (J.Amer.Chem.Soc., 1936, 58, 2296), who had studied the ultra-violet absorption spectra of 2,4,6,2',4',6'-hexachloro biphenyl and bimesityl in alcohol solution. It was especially noticeable in the chlorine compound that the bands had very sharp edges on the shorter wave-length side. The absorption curves of the corresponding benzene derivatives, 1,3,5-trichlorobenzene and mesitylene are shown by them for comparision, where it would be noticed that the band maxima of the most intense bands in the benzene derivative correspond to similar ones in the biphenyl compound, which are displaced towards the visible region of the spectrum. This shift is small and fairly constant for the chloro compounds, but larger for those with methyl groups. The extinction coefficient of the band maxima of the biphenyl derivative is two or three times that of the corresponding benzene, indicating that the absorption is nearly additive for the two benzene rings.

Williamson and Rodebush (J.Amer.Chem.Soc.,1941, 63, 3018) studied the effect of substituent groups upon the absorption of biphenyl and concluded that excellent correlation has been obtained in most cases between the possible resonance structures and values for extinction coefficient and wave-length of the maximum absorption. Remington (J. Amer. Chem. Soc., 1945, 67, 1838) examined the effect of steric hindrance on the absorption spectra of dimethylaniline, and concluded that molecular planarity was a requirement for the characteristic absorption of dimethylaniline.

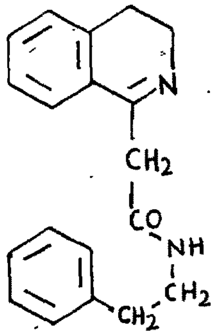
Corley and Blout (loc.cit.) studied the absorption spectra of β-naphthol, β-naphthylamine, 2-amino-2'-hydroxy-1,1'-di-naphthylmethane and bis-(2-hydroxy-1-naphthyl)-methane, and concluded that there is a small degree of interaction between the amine and the phenol at very dilute concentrations (10^{-3}M to 10^{-5}M). The spectrum of the dinaphthylmethane is given by them for comparision with that of the equimolecular mixture of β-naphthol and β-naphthylamine, and that of bis-(2-hydroxy-1-naphthyl)-

methane. The curve of the dinaphthylmethane is seen to be nearly identical with that of the dinaphthol (effect of the methylene linkage), and that of β-naphthol plus β-naphthylamine (effect of coexistant amino and phenol functions).

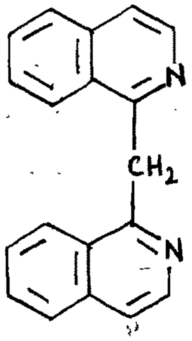
Ghosh, Ganguly and Bhattacharya (loc.cit.) have recorded that malon di-β-phenethylamide underwent the Bischler-Napieralski cyclisation in the presence of P_2O_5 to yield 1:1'-methylene-bis-3:4-dihydroisoquinoline (I) along with a small quantity of 1-(N-β-phenethylacetamido)-3:4-dihydroisoquinoline (II). Dehydrogenation of methylene-bis-compound over Pd-C leads to the formation of the fully aromatised isoquinoline (III). For studying the presence of conjugation in the compound (I), the absorption spectra of (I), its dehydrogenated product (III) and that of (II) have been studied. They found that, the absorption spectrum of (III) and that of (II) resembled respectively those of the normal isoquinoline derivatives, e.g. 1-methyl-3:4-dihydroisoquinoline and 1-benzyl-3:4-dihydroisoquinoline.



(I)



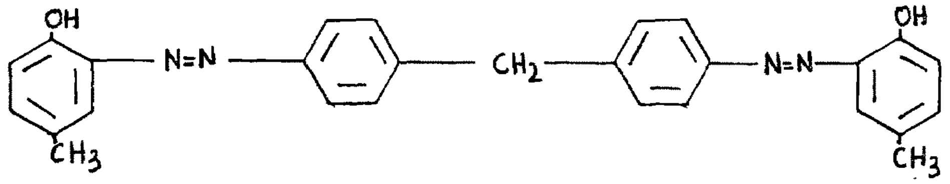
(II)



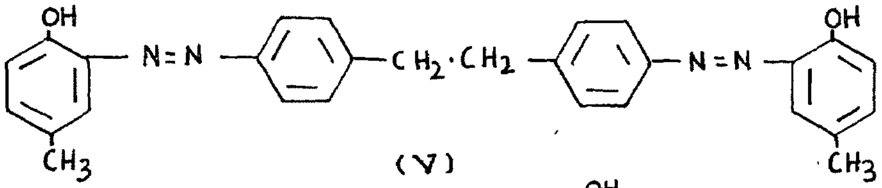
(III)

Piper and Brode (J.Amer. Chem. Soc., 1935, 57, 135) studied the relation between the absorption spectra and the chemical constitution of dyes. In a study of molecules containing two chromophores they have shown that the connecting of the two chromophores by a methylene ($-CH_2-$) or ethylene ($-CH_2-CH_2-$) linkage gives almost complete insulation of the separate chromophores, since the absorption spectra of the molecule with two chromophores is nearly indentical with the summation of the absorption spectra of two separate molecules, each containing one of the chromophores. With compounds involving two chromophores in the same molecule, it has been demonstrated that certain linkage such as $-CH_2-$, $-CH_2.CH_2-$, $-(CH_2)n-$ etc.act as insulating pads between the two resonating groups and fail to transmit any effect from one chromophore to another. In conjugation coupling there appears to be a multiplication effect resulting in a bathochromic and hyperchromic effect.

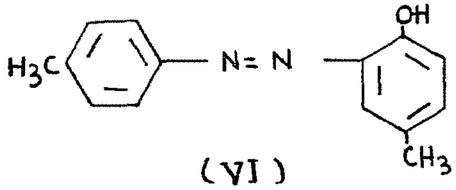
It is quite obvious from the absorption spectra data that in all the solvents studied, the para-coupled diazo dyes, which are separated by $-CH_2-$ or $-CH_2.CH_2-$ between the centre aromatic groups (IV and V), have chromophores which are quite independent of each other, in that their absorption spectra curves are almost indentical with the corresponding component monoazo dye absorption curve (twice the absorption value of dye VI).



(IV)



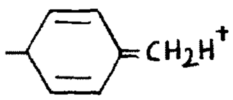
(V)

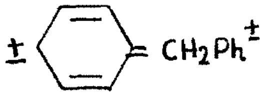


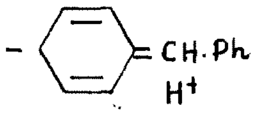
(VI)

Braude (J.Chem.Soc., 1949,1902) pointed out that one of the basic principles which has long been accepted in the empirical interpretation of ultra-violet light absorption is that the absorption due to isolated chromophores is additive ; i.e., that the interaction between the unsaturated electrons of groups separated by one or more saturated carbon atoms is too weak to affect the spectral properties. He studied the spectra of the type, $X.(CH_2)n.Y$, where X and Y are single chromophores such as $-C{=}C-$, $-C{\equiv}C-$, $-C{=}O-$, and $-COOH$,. Among the few available examples of this type are diallyl, cyclohexane-1:4-dione, and succinic acid, which show ultraviolet absorption corresponding very nearly to that of two propylene, acetone and acetic acid molecules respectively. Ramart-Lucas (Bull.Soc.chem., 1932, <u>51</u>, 965 ; ibid., 1943, <u>10</u>, 13) formulated the rule that in compounds of the type $Ph.(CH_2)_nY$, when n = 2 or greater, the absorption is practically indistinguishable from that of an equimolecular mixture of PhEt and Et.Y, but that when n = I, the intensities of absorption are somewhat enhanced though the wave-length of the band remains unchanged.

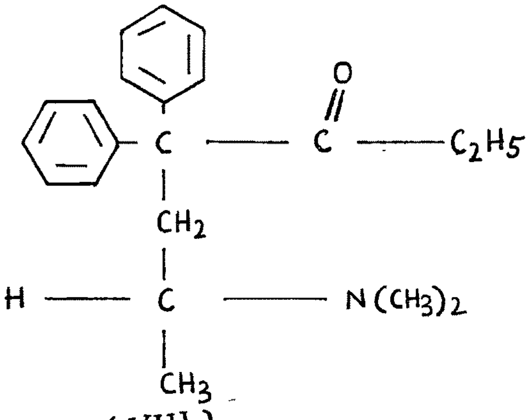
This considerable deviations from additivity in the ultra-violet light absorption of certain systems of the type $X-CH_2.Y$, are due to electronic interaction between the two phenyl groups. Such interaction must take place either by way of the intervening saturated $-CH_2-$ group, or else spatially between the phenyl groups belonging to the same or different molecules. Intermolecular interaction is excluded in view of the low concentration employed in absorption measurements. Intramolecular spatial interaction between the two sets of electrons also seems unlikely in view of the distance between, and the relative position of the phenyl groups. It therefore appears probable that interaction takes place by way of the intervening methylene group, a conclusion which can be expressed in terms of contributions from resonance forms such as (VIIa) or (VII b).


(VII)


(VIIa)


(VIIb)

Kumler, Strait and Alpen (J. Amer. Chem. Soc., 1950, 72, 1463) concluded that if in absorption spectroscopy two chromophores separated by one or more saturated carbon atoms absorb independently and the absorption of the compound was the sum of the absorption of the individual chromophores, in a compound like methadon (VIII) the absorption should show the additive effect of diphenylmethane plus that of a ketone. This however did not agree with their observations.



(VIII)

They further measured the absorption spectra of some α-phenyl carbonyl compounds including phenyl acetaldehyde, phenylacetone, phenylmethylacetone, phenyl acetic acid and diphenyl acetic acid. Here the interaction between the carbonyl group and the phenyl group was shown to take place through the saturated α-carbon atom. An explanation in terms of no-bond resonance has been given for the phenomenon. This behaviour indicates that two chromophore groups do not always act independently when separated by a saturated carbon atom and that some resonance interaction takes place through such an atom.

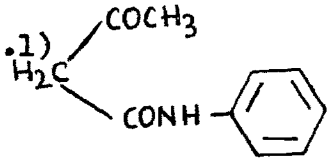
In the present investigation of Part V the ultra violet absorption spectra of a number of acetoacet arylamides, hydroxyquinolines and their respective methylene bis-derivatives have been studied to observe the insulation effect in a number of bis-compounds, in which one half of the molecule is a replica of the other half, bridged by a reactive methylene $-CH_2-$ group. Friedel and Orchin (loc.cit.) have drawn the attention to this effect in a number of simple cases, but none of the compounds mentioned has a bis-derivative. It was, therefore, of interest to examine the pairs of a number of compounds of the mono-and the bis-derivatives, which were available for study.

The following two series of (i) acetoacet arylamides and their corresponding (ii) methylene bis-(acetoacetarylamide derivatives), have been therefore prepared and their absorption spectra in the ultra violet (plates I:-IV) studied:- P = Plate ; C = Curve

(i) Acetoacet arylamides :

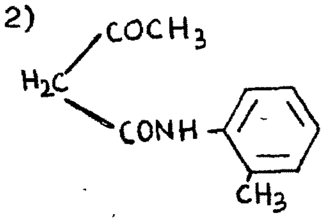
(1) acetoacetanilide

(P.I ; C.1)



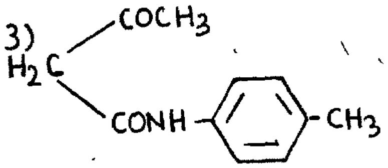
(2) acetoacet-o-toluidide

(P.I ; C.2)



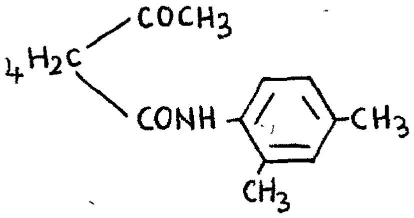
(3) acetoacet-p-toluidide

(P.II ; C.3)



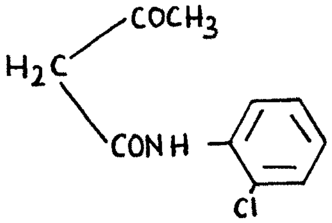
(4) acetoacet-1:2:4-xylidide

(P.II ; C.4



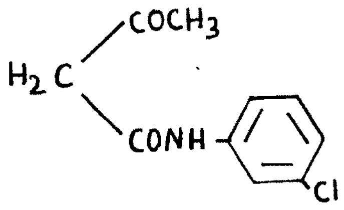
(5) acetoacet-o-chloroanilide

(P.III ; C.5)



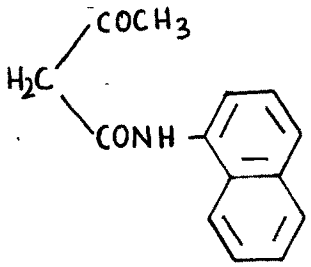
(6) acetoacet-m-chloroanilide

(P.III ; C.6)



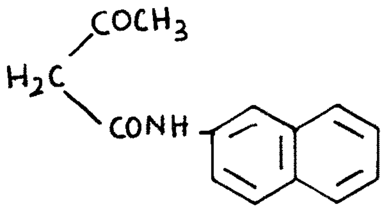
(7) acetoacet-α-naphthylamide

(P.IV ; C.7)



(8) acetoacet-β-naphthylamide

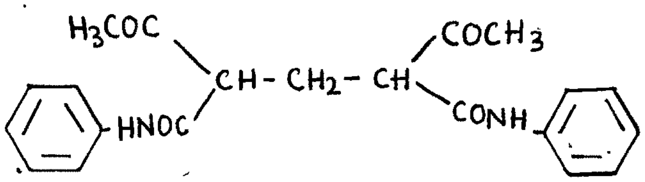
(P.IV ; C.8)



(ii) <u>Methylene bis-(-acetoacetarylamides</u>) :

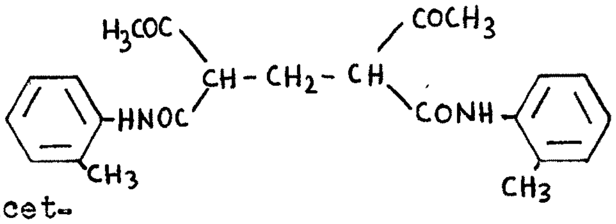
(1') methylene bis-(acetoacet-
anilide)

(P.II ; C.1′)



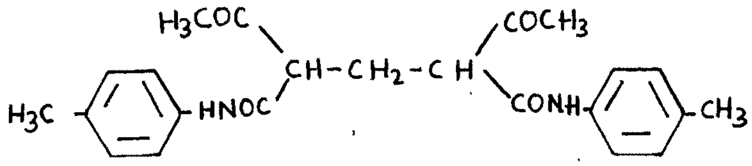
(2') methylene bis-(acetoacet-
o-toluidide)

(P.I ; C.2')



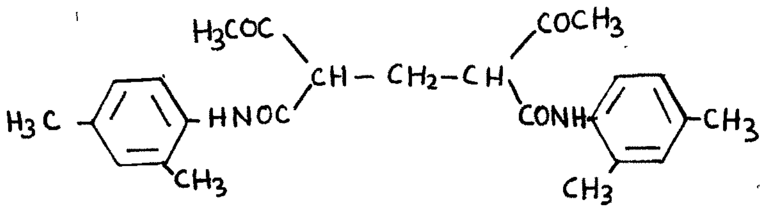
(3') methylene bis-(acetoacet-
p-toluidide)

(P.II ; C.3')



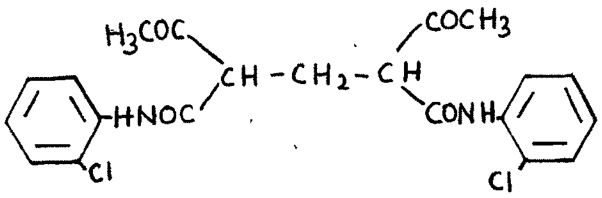
(4') methylene bis-(acetoacet-
1:2:4-xylidide)

(P.II ; C.4')



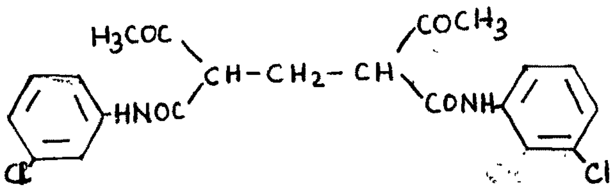
(5') methylene bis-(acetoacet-
o-chloroanilide)

(P.III ; C.5')



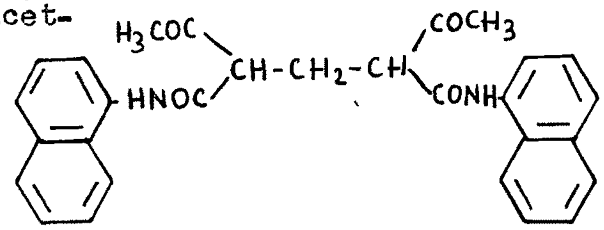
(6') methylene bis-(acetoacet-
m-chloroanilide)

(P.VIII; C.6')



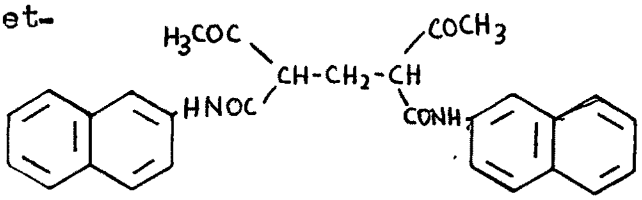
(7') methylene bis-(acetoacet-
α-naphthylamide)

(P.IV ; C.7')



(8') methylene bis-(acetoacet-β-naphthylamide)

(P.IV ; C.8')

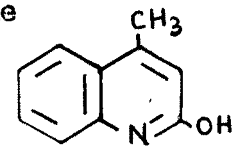


Similarly the following two series of (a) 2-hydroxyquinolines and their corresponding (b) 3:3'-methylene bis-quinoline derivatives have been prepared and their absorption spectra in the ultra-violet, (plates V-VIII) studied :

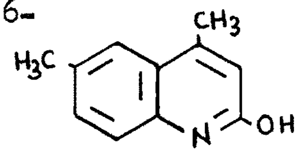
(a) Hydroxyquinolines :

(1) 2-hydroxy-4-methyl-quinoline

(P.V ; C.1)

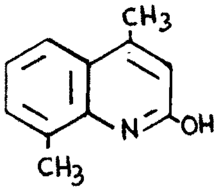


(2) 2-hydroxy-4,6-dimethyl-quinoline



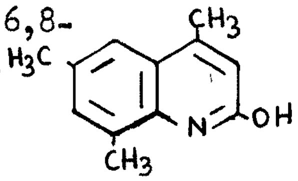
(P.V ; C.2)

(3) 2-hydroxy-4,8-dimethyl-quinoline



(P.VI ; C.3)

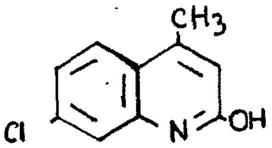
(4) 2-hydroxy-4,6,8-trimethyl-quinoline



(P.VI ; C.4)

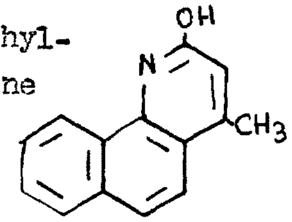
(5) 2-hydroxy-4-methyl-
7-chloro-
quinoline

(P.VII ; C.5)



(6) 2-hydroxy-4-methyl-
benzoquinoline
(7:8)

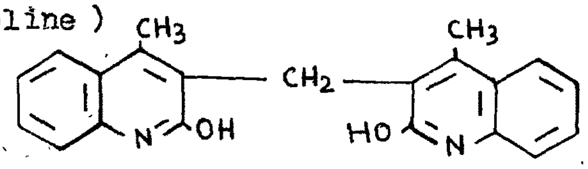
(P.VIII ; C.6)



(b) <u>Methylene bis-hydroxyquinolines</u> :

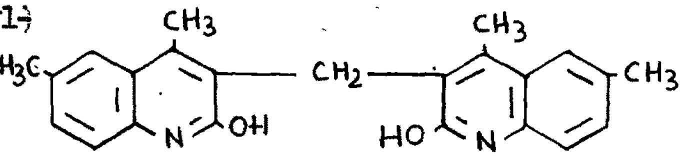
(1') 3,3'-methylene
bis-(2-hydroxy-
4-methyl-)quinoline)

(P.V ; C.1')



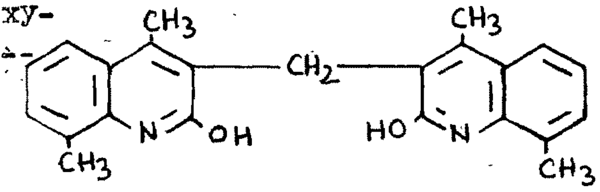
(2') 3,3'-methylene
bis-(2-hydroxy-
4,6-dimethyl-)
quinoline)

(P.V ; C.2')



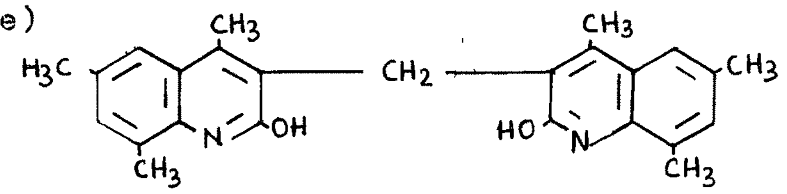
(3') 3,3'-methylene
bis-(2-hydroxy-
4:8-dimethyl-
quinoline)

(P.VI ; C.3')



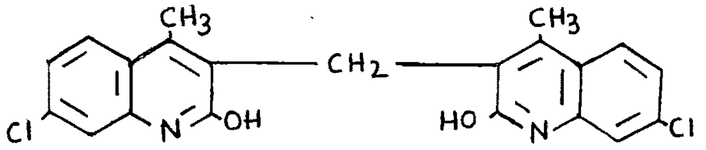
(4') 3,3'-methylene bis-(2-hydroxy-4,6,8-trimethyl-quinoline)

(P.VI ; C.4')



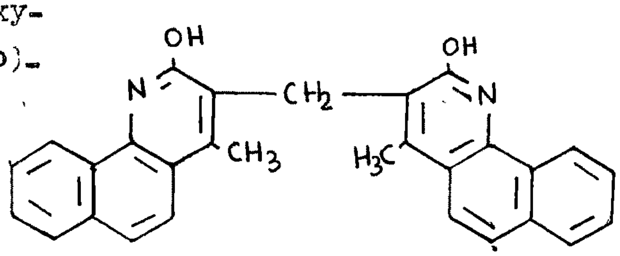
(5') 3,3'-methylene bis-(2-hydroxy-4-methyl-7-chloro)quinoline)

(P.VII ; C.5')



(6') 3,3'-methylene bis-(2-hydroxy-4-methyl-benzo)-quinoline)(7:8)

(P.VIII ; C.6')



The extinction coefficient values (log.E) of the above mentioned methylene bis(-acetoacet arylamides) and of acetoacet arylamides as well as of the methylene bis-(-2-hydroxy-4-methylquinolines) and of 2-hydroxy-4-methyl-quinolines are shown in Table 1-a and in Table 5-a respectively. Thus, the curves on plates I to IV are from the results of Table 1-a ; whereas those on plates V to VIII are related to Table 5-a. The results embodied in Tables 2-a and 3-a indicate respectively the log E difference and log E ratio (absorption intensity) between the bis-compounds relative to the corresponding mono derivatives ; whereas Tables 6-a and 7-a respectively show the absorption intensity in log E difference and in log E ratio ; similarly of bis-quinolines relative to their corresponding mono derivatives.

The mean factors of the values of log E difference and log E ratio respectively at definite ranges of wave lengths, calculated in Tables 4-a and 8-a, indicate the average hyperchromic effect, shown by the bis-compounds relative to the corresponding mono derivatives. It would be noticed that the bathochromic or the hypsochromic effects (i.e. wave length shift towards longer wave length and shorter wave length respectively) are comparatively very small in the pairs examined. As preliminary observation which may be quantitatively established, it may be said that a definite hyperchromic effect is shown by the rise in the absorption intensity of the bis-compounds. Accordingly, from the results of intensity differences in Tables 4-a and 8-a of each pair of compounds from minimum to maximum in the two series, may be placed in the following order :

<u>Acetoacet-arylamide series</u> :- 3' : 3 ; 4' : 4 ; 7' : 7 ; 6' : 6 ; 1' : 1 ; 8' : 8 ; 5' : 5 ; and 2' : 2 (Plates I - IV)

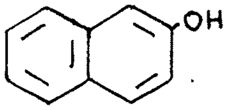
<u>Hydroxyquinoline series</u> :- 6' : 6 ; 3' : 3 ; 2' : 2 ; 5' : 5 ; 4' : 4 and 1' : 1 (Plates V - VIII)

These results indicate that a considerable increase in the absorption intensity takes place, when certain groups like $-CH_3$,-Cl etc. are substituted in the ortho position in presence of another group in the p-position in benzene or in quinoline nucleus. Similar systematic difference due to the presence and proximity of certain groups would be observed on the comparision of the hyperchromic effect with the corresponding pairs of compounds in both the series. Unfortunately, the data is lacking on very simple compounds having identical absorption groups, but joined by one or more $-CH_2-$ bridges, as for examples members in the series of simple dibasic acids, such as, oxalic, malonic, succinic, glutaric and adipic or a large number of their substituted amides, could be quoted. Similar compounds in the aromatic series also would be interesting as their absorption intensities would be considerably greater.

As a preliminary attempt in this direction a search is being made and the following five known pair of compounds, not necessarily interrelated, have been studied here for comparision.

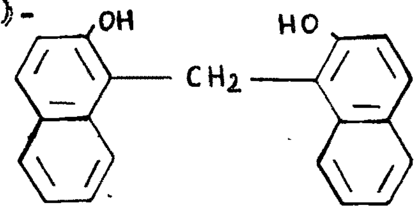
(1) β-naphthol

(P. IX ; C.1)



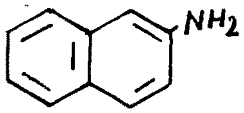
(1') Bis-(2-hydroxy-1-naphthyl)-methane

(P. IX ; C.1')



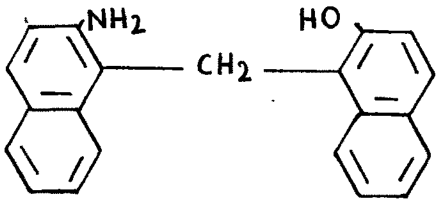
(2) β-naphthylamine

(P.X ; C.2)



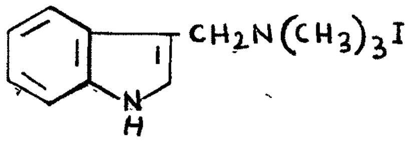
(2') 2-Amino-2'-
hydroxy-1-1'-
dinaphthyl
methane

(P.X ; C.2')



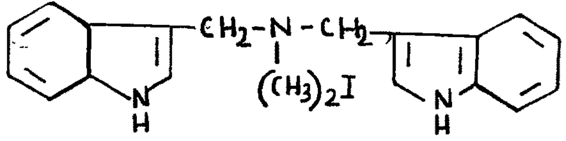
(3) Grammine
methiodide

(P.XI ; C.3)



(3') 3,3'-Bis-
indolylmethyl
dimethyl
ammonium iodide

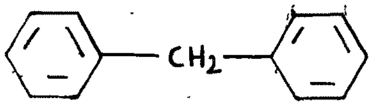
(P.XI ; $C._3$')



(4) Benzene

(P.XII ; C.4)

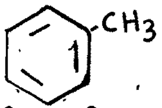
(4') Diphenylmethane



(P.XII ; C.4')

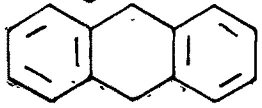
(5) Toluene

(P.XIII ; C.5)



(5') 9,10-Dihydro-
anthracene

(P.XIII ; C.5')



The extinction coefficient values (log E) of the above known pairs of compounds from 1-1' to 5-5' are shown in Table 9-a and the curves are given on plates IX,X,XI, XII and XIII respectively. The corresponding values of absorption difference and their ratio in the intensity of each pair of compound respectively are shown in Tables 10-a and 11-a from which the mean factors of the values of the intensity of absorption in log E difference and in log E ratio at different ranges of wave lengths are calculated in Table 12-a as before. It would be noticed in this case that the maximum hyperchromic effect is shown by the simpler derivative of benzene and toluene, while the effect is smaller in the case of rest of the pairs and more comparable to the effect shown by the compounds investigated in the present work. It is obvious, however, that for a quantitative insight into the phenomenon of the hyperchromic effect, a detailed and systematic study of the absorption spectra of a large number of related compounds is necessary. But, the hyperchromic effect, seen from the increased absorption intensity and the trend in the extinction coefficient of absorption bands in the bis-series of compounds, when compared with those of their corresponding mono derivatives, furnishes an interesting subject for further studies.

<u>Reference of the pair of absorption curves</u> :

Plate I : Curves 1-1' refer to respectively acetoacet phenylamide and its methylene bis-derivative ;

2-2'-refer to respectively acetoacet-o-toluidide and its methylene bis-derivative.

Plate II: Curves 3-3'-refer to respectively acetoacet-p-toluidide and its methylene bis-derivative ;
4-4'-refer to respectively acetoacet-1:2:4-xylidide and its methylene bis-derivative.

Plate III: Curves 5-5'-refer to respectively acetoacet-o-chloroanilide and its methylene bis-derivative ;
6-6'-refer to respectively acetoacet-m-chloroanilide and its methylene bis-derivative.

Plate IV: Curves 7-7'-refer to respectively acetoacet-α-naphthylamide and its methylene bis-derivative ;
8-8'-refer to respectively acetoacet-β-naphthylamide and its methylene bis-derivative.

Plate V: Curves 1-1'-refer to respectively 2-hydroxy-4-methylquinoline and its methylene bis-derivative ;
2-2'-refer to respectively 2-hydroxy-4,6-dimethylquinoline and its methylene bis-derivative.

Plate VI: Curves 3-3'-refer to respectively 2-hydroxy-4,8-dimethylquinoline and its methylene bis-derivative ;
4-4'-refer to respectively 2-hydroxy-4:6:8-trimethylquinoline and its methylene bis-derivatives.

Plate VII: Curves 5-5'-refer to respectively 2-hydroxy-4-methyl-7-chloroquinoline and its methylene bis-derivative.

Plate VIII: Curves 6-6'-refer to respectively 2-hydroxy-4-methylbenzoquinoline (7:8) and its methylene bis-derivative.

Note on the preparation of bis-and mono series of compounds :

Acetoacet arylamides have been prepared according to the method of Ewins and King (loc.cit.) as modified by Naik et al. (loc.cit.). The methylene bis-(acetoacet arylamides) were synthesised by condensing the corresponding acetoacet arylamides with sodium hydroxy methane sulphonate (Mehta and Patel loc.cit.). Ewins and King (loc.cit.) further cyclised the acetoacet arylamides to form 2-hydroxy-4-methylquinolines, su using concentrated sulphuric acid and the present method involved the use of a mixture of acetic anhydride and concentrated sulphuric acid, as was employed by Bangdiwala and Desai (loc.cit.) to obtain 4-hydroxy-2-methylquinolines. The 3:3'-methylene bis-(2-hydroxy-4-methylquinolines) part IV have been prepared by cyclisation of methylene bis-(acetoacet arylamides) using a mixture of acetic anhydride and concentrated sulphuric acid (Mehta and Patel loc.cit.).

Table 1-a

Extinction coefficient of methylene bis-(acetoacet arylamides) and of acetoacet arylamides.

	Log E		Log E		Log E		Log E	
A°	1'	1	2'	2	3'	3	4'	4
2400	-	-	4.854	3.974	4.460	4.227	4.383	4.075
2600	4.305	3.976	4.530	3.712	4.441	4.197	4.217	3.825
2800	3.983	3.677	4.583	3.621	4.170	3.868	3.978	3.660
3000	3.755	3.361	4.378	3.387	3.894	3.583	3.703	3.385
3200	3.618	3.075	4.332	3.232	3.761	3.355	3.546	3.210
3400	3.524	2.962	4.240	3.130	3.627	3.270	3.446	3.140
3600	3.412	2.850	3.987	3.046	3.473	3.170	3.330	3.030
3800	3.338	2.793	3.851	2.960	3.415	3.078	3.290	2.935
4000	3.263	2.728	3.761	2.900	3.377	3.017	3.251	2.857

Table 1-a (Contd.)

A°	Log E 5'	5	Log E 6'	6	Log E 7'	7	Log E 8'	8
2400	-	-	4.465	4.325	-	-	-	-
2600	4.638	3.988	4.360	4.210	4.207	3.832	4.841	4.134
2800	4.273	3.648	4.107	3.787	4.355	3.980	4.722	4.162
3000	4.018	3.334	3.863	3.532	4.338	3.948	4.590	4.045
3200	3.887	3.158	3.709	3.175	4.140	3.750	4.286	3.706
3400	3.186	3.078	3.523	3.075	3.725	3.420	4.150	3.600
3600	3.688	2.961	3.397	2.965	3.593	3.180	4.047	3.437
3800	3.628	2.875	3.305	2.898	3.491	3.044	4.003	3.193
4000	3.631	2.800	3.226	2.846	3.450	2.952	3.960	3.072

Table 2-a

Log E difference between methylene bis-(acetoacetarylamides) and acetoacetarylamides.

	Log E diff. 1'-1	Log E diff. 2'-2	Log E diff. 3'-3	Log E diff. 4'-4	Log E diff. 5'-5	Log E diff. 6'-6	Log E diff. 7'-7	Log E diff. 8'-8
A°	Plate I		Plate II		Plate III		Plate IV	
2400	-	0.880	0.233	0.308	-	0.140	-	-
2600	0.330	0.828	0.244	0.392	0.650	0.150	0.375	0.707
2800	0.306	0.962	0.302	0.318	0.625	0.320	0.375	0.560
3000	0.394	0.991	0.311	0.318	0.684	0.331	0.390	0.545
3200	0.543	1.100	0.406	0.336	0.729	0.534	0.390	0.580
3400	0.562	1.100	0.357	0.306	0.708	0.448	0.305	0.550
3600	0.562	0.941	0.303	0.300	0.727	0.432	0.413	0.610
3800	0.545	0.891	0.337	0.355	0.753	0.407	0.447	0.810
4000	0.535	0.861	0.360	0.394	0.831	0.380	0.498	0.888

Table 3-a

Log E ratio between methylene bis-(acetoacetarylamides) and acetoacetarylamides.

A°	Log E ratio. 1'/1	Log E ratio. 2'/2	Log E ratio. 3'/3	Log E ratio. 4'/4	Log E ratio. 5'/5	Log E ratio. 6'/6	Log E ratio. 7'/7	Log E ratio. 8'/8
	Plate I		Plate II		Plate III		Plate IV	
2400	-	1.22	1.054	1.090	-	1.030	-	-
2600	1.08	1.22	1.057	1.080	1.161	1.035	1.096	1.170
2800	1.09	1.26	1.076	1.086	1.172	1.099	1.094	1.135
3000	1.11	1.29	1.086	1.094	1.205	1.092	1.096	1.135
3200	1.17	1.34	1.122	1.104	1.230	1.167	1.104	1.156
3400	1.19	1.35	1.109	1.096	1.230	1.146	1.080	1.152
3600	1.23	1.31	1.096	1.099	1.245	1.146	1.130	1.178
3800	1.19	1.30	1.110	1.119	1.262	1.140	1.146	1.253
4000	1.19	1.30	1.119	1.138	1.294	1.132	1.167	1.288

Table 4-a

Mean factors of Log E difference and of Log E ratio between methylene bis-(acetoacet arylamides) and acetoacet arylamides at different ranges of wave lengths.

Log E diff.	2400-2800 A°	2800-3200 A°	3200-3600 A°	3600-4000 A°	
(1'-1)	0.318	0.399	0.540	0.543	
(2'-2)	0.890	1.000	1.050	0.898	
(3'-3)	0.290	0.306	0.322	0.333	
(4'-4)	0.339	0.323	0.313	0.350	
(5'-5)	0.637	0.678	0.721	0.770	
(6'-6)	0.203	0.395	0.471	0.406	
(7'-7)	0.375	0.385	0.369	0.452	
(8'-8)	0.634	0.561	0.580	0.769	
Log E ratio.	**2400-2800 A°**	**2800-3200 A°**	**3200-3600 A°**	**3600-4000 A°**	**Average of intensity ratio**
(1'/1)	1.085	1.125	1.120	1.200	1.138
(2'/2)	1.230	1.326	1.330	1.300	1.296
(3'/3)	1.062	1.096	1.109	1.108	1.093
(4'/4)	1.085	1.099	1.100	1.109	1.098
(5'/5)	1.660	1.200	1.235	1.266	1.217
(6'/6)	1.054	1.119	1.153	1.139	1.114
(7'/7)	1.095	1.098	1.104	1.147	1.111
(8'/8)	1.122	1.142	1.162	1.236	1.165

Table 5-a

Extinction coefficient of methylene bis-(hydroxyquinolines) and of hydroxyquinolines.

	Log E		Log E		Log E		Log E		Log E		Log E	
A°	1'	1	2'	2	3'	3	4'	4	5'	5	6'	6
2400	-	-	4.640	4.200	-	-	-	-	-	-	4.587	4.554
2600	4.691	3.914	4.495	3.853	4.531	4.150	4.430	3.749	4.619	3.955	4.384	4.337
2800	4.544	3.774	4.410	3.890	4.516	4.165	4.517	3.834	4.642	4.020	4.583	4.340
3000	4.370	3.607	4.203	3.504	4.316	3.950	4.303	3.419	4.425	3.760	4.232	3.935
3200	4.435	3.837	4.190	3.750	4.356	3.978	4.287	3.583	4.564	3.974	4.098	3.775
3400	4.293	3.725	4.100	3.797	4.286	3.901	4.380	3.680	4.490	3.936	4.045	3.752
3600	3.842	2.773	3.790	3.255	3.900	3.550	4.077	3.347	3.870	3.150	4.016	3.729
3800	3.755	2.690	3.650	2.895	3.783	3.450	3.645	2.808	3.768	3.063	3.866	3.216
4000	3.755	2.726	3.557	2.819	3.701	3.362	3.597	2.728	3.731	3.016	3.627	3.016

Table 6-a

Log E difference between methylene bis-(hydroxyquinolines) and hydroxyquinolines.

	Log E diff. 1'-1	Log E diff. 2'-2	Log E diff. 3'-3	Log E diff. 4'-4	Log E diff. 5'-5	Log E diff. 6'-6
A°	Plate V		Plate VI		Plate VII	Plate VIII
2400	-	0.440	-	-	-	0.033
2600	0.777	0.642	0.381	0.681	0.664	0.047
2800	0.770	0.520	0.351	0.683	0.622	0.243
3000	0.763	0.649	0.366	0.884	0.665	0.295
3200	0.598	0.440	0.378	0.704	0.590	0.323
3400	0.568	0.403	0.385	0.700	0.554	0.293
3600	1.069	0.535	0.350	0.730	0.720	0.287
3800	1.065	0.755	0.333	0.837	0.705	0.650
4000	1.029	0.738	0.339	0.869	0.715	0.611

Table 7-a

Log E ratio between methylene bis-(hydroxyquinolines) and hydroxyquinolines.

	Log E ratio. 1'/1	Log E ratio. 2'/2	Log E ratio. 3'/3	Log E ratio. 4'/4	Log E ratio. 5'/5	Log E ratio. 6'/6
A°	Plate V		Plate VI		Plate VII	Plate VIII
2400	-	1.104	-	-	-	1.007
2600	1.198	1.164	1.091	1.180	1.167	1.010
2800	1.202	1.132	1.084	1.352	1.153	1.054
3000	1.211	1.200	1.091	1.260	1.175	1.074
3200	1.160	1.117	1.094	1.194	1.148	1.084
3400	1.151	1.080	1.072	1.190	1.140	1.076
3600	1.384	1.164	1.119	1.220	1.227	1.076
3800	1.393	1.260	1.096	1.297	1.230	1.202
4000	1.377	1.262	1.100	1.320	1.236	1.200

Table 8-a

Mean factors of Log E difference and of Log E ratio between methylene bis-(hydroxyquinolines)and hydroxyquinolines at different ranges of wave lengths.

Log E diff.	2400-2800 A°	2800-3200 A°	3200-3600 A°	3600-4000 A°
(1'-1)	0.770	0.708	0.735	1.054
(2'-2)	0.527	0.553	0.458	0.676
(3'-3)	0.366	0.365	0.371	0.340
(4'-4)	0.682	0.757	0.711	0.812
(5'-5)	0.643	0.626	0.621	0.713
(6'-6)	0.161	0.287	0.301	0.516

Log E ratio.	2400-2800 A°	2800-3200 A°	3200-3600 A°	3600-4000 A°	Average of intensity ratio
(1'/1)	1.200	1.191	1.231	1.384	1.251
(2'/2)	1.133	1.149	1.120	1.229	1.158
(3'/3)	1.087	1.093	1.095	1.105	1.095
(4'/4)	1.266	1.268	1.168	1.279	1.247
(5'/5)	1.160	1.158	1.172	1.231	1.180
(6'/6)	1.023	1.080	1.078	1.158	1.084

Table 9-a

Extinction coefficient of some known bis- and simple compounds.

	Plate IX		Plate X		Plate XI		Plate XII		Plate XIII	
A°	1'	1	2'	2	3'	3	4'	4	5'	5
2200	-	-	-	-	-	-	-	-	4.15	2.70
2300	4.95	4.95	4.70	4.60	4.35	4.20	2.70	1.15	2.60	1.15
2400	4.90	3.90	4.85	4.80	3.60	3.30	2.15	1.70	2.10	1.70
2500	3.60	3.50	4.45	4.30	3.70	3.40	2.40	2.30	2.60	2.10
2600	3.70	3.60	4.05	3.60	4.10	3.70	2.70	2.20	2.90	2.40
2700	3.85	3.72	3.90	3.70	4.15	3.80	2.40	0.70	3.00	2.25
2800	3.95	3.55	4.00	3.80	4.00	3.75	-	-	-	-
2900	3.30	3.10	3.60	3.00	3.80	3.10	-	-	-	-
3000	3.30	3.00	3.80	2.70	-	-	-	-	-	-
3200	3.60	3.25	3.55	3.10	-	-	-	-	-	-
3400	3.80	2.50	3.75	3.25	-	-	-	-	-	-
3600	-	-	3.30	2.90	-	-	-	-	-	-
3800	-	-	-	-	-	-	-	-	-	-

Table 10-a

Log E difference between the known bis- and simple compounds.

	Log E diff. 1'-1	Log E diff. 2'-2	Log E diff. 3'-3	Log E diff. 4'-4	Log E diff. 5'-5
A°	Plate IX	Plate X	Plate XI	Plate XII	Plate XIII
2200	-	-	-	-	1.45
2300	1.0	0.10	0.15	1.55	1.45
2400	1.0	0.05	0.30	0.45	1.40
2500	0.10	0.15	0.30	0.10	0.50
2600	0.10	0.45	0.40	0.50	0.50
2700	0.13	0.20	0.35	1.70	0.75
2800	0.40	0.20	0.25	-	-
2900	0.20	0.60	0.70	-	-
3000	0.30	1.10	-	-	-
3200	0.35	0.45	-	-	-
3400	1.30	0.50	-	-	-
3600	-	0.60	-	-	-

Table 11-a

Log E ratio between the known bis- and simple compounds.

	Log E ratio. 1'/1	Log E ratio. 2'/2	Log E ratio. 3'/3	Log E ratio. 4'/4	Log E ratio. 5'/5
A°	Plate IX	Plate X	Plate XI	Plate XII	Plate XIII
2200	-	-	-	-	1.54
2300	1.00	1.02	1.03	2.34	2.26
2400	1.25	1.01	1.09	1.26	1.23
2500	1.02	1.34	1.09	1.04	1.24
2600	1.02	1.12	1.10	1.22	1.20
2700	1.03	1.05	1.09	3.43	1.33
2800	1.11	1.05	1.06	-	-
2900	1.07	1.20	1.22	-	-
3000	1.10	1.40	-	-	-
3200	1.10	1.44	-	-	-
3400	1.52	1.15	-	-	-
3600	-	1.14	-	-	-

Table 12 -a

Mean factors of Log E difference and of Log E ratio between the known -bis and simple compounds at different ranges of wave-length

Log E diff.	2200-2400 A°	2300-2500 A°	2400-2600 A°	2500-2700 A°	2700-3000 A°	3000-3400 A°	
(1'-1)	-	0.70	0.40	0.11	0.26	0.65	
(2'-2)	-	0.10	0.15	0.23	0.73	0.70	
(3'-3)	-	0.23	0.33	0.33	0.43	-	
(4'-4)	-	0.70	0.35	0.90	-	-	
(5'-5)	1.43	1.12	0.80	0.58	-	-	
Log E ratio	**2200-2400 A°**	**2300-2500 A°**	**2400-2600 A°**	**2500-2700 A°**	**2700-3000 A°**	**3000-3400 A°**	**Average of intensity ratio**
(1'/1)	-	1.09	1.09	1.02	1.08	1.24	1.104
(2'/2)	-	1.12	1.16	1.17	1.17	1.33	1.150
(3"/3)	-	1.07	1.09	1.09	1.12	-	1.092
(4'/4)	-	1.55	1.17	1.90	-	-	1.540
(5'/5)	1.68	1.58	1.23	1.30	-	-	1.450