Present Work - Results and Discussion

Part-I
Several methods are known in literature for the construction of benzo(k)phenanthridine system. The first method was due to Mills and Schofield and it involved an Ullmann reaction between 1-iodonaphthalene and an o-nitrohalobenzene, leading to 1-(2-nitrophenyl)naphthalene (77), as the starting point.

\[ \text{I} + \text{Br} \xrightarrow{\text{NO}_2} \text{77} \]

1. Reduction
2. Acetylation

\[ \text{POCl}_3 \xrightarrow{\text{SnCl}_4} \]

\[ \text{6} \]
The nitro compound (77) was reduced and the resulting amino compound was acylated with acetic anhydride to give 78. The compound 78 on heating with a mixture of phosphoryl chloride and stannic chloride gave the benzo(k)phenanthridine (6, R = H). The disadvantage in this method is the low yield accessibility of the starting intermediate viz., the Ullmann reaction product 77. Since only a few o-nitro halobenzenes are known, there is a corresponding limitation in its generality.

Recently, Boyer and Patel,\textsuperscript{66} reported that cyclization of 1-(2-formamidophenyl)naphthalene (78, R = H), resulted in a 20\% yield of the parent benzo(k)phenanthridine (6), the major product being the seven membered ring compound 79.
In another method, Mills and Schofield reacted indeno(2,1-c)quinolinone (80) with diazomethane which resulted in a ring expansion to give the methoxy benzophenanthridine 81 or 82. The method lacked practicality because of the cumbersomeness of the procedure involved in the preparation of 80 as well as its conversion, to 81 or 82.

\[
\text{In the year 1957, Hey and co-workers prepared 4-aminomethyl-2-naphthanilide (83) and subjected it to Pschorr ring closure (diazotization/cu powder/\Delta). Among the products that had resulted the benzo(k)phenanthridone (84) was found to be one, of course, in a poor yield.}
\]
Although they failed to identify the product (only the m.p. was reported), Keene and Schofield\textsuperscript{68} obtained the N-methyl-benzo(k)phenanthridone (84) by a different sequence (described in the sequel) and found it to be identical with 84 which eluded Hey and coworkers' attempt in identification.

Hey and co-workers\textsuperscript{69} also synthesised N-methyl-N-\(\beta\)-naphthoylphenylenediamine (85) and subjected it to a Pschorr ring closure. They assumed the product to be 84. Workers from the same laboratory, reinvestigated the reaction and
proved the result to be erroneous. They reinvestigated the Pschorr ring closure of 83 and attested the contention of Keene and Schofield\(^68\) that one of the products resulted from it, is N-methyl-benzo(k)phenanthridone (84). Apart from the meagreness of the yield of 84, obtainable from the above procedure, the preparation of the starting intermediate viz., 1-nitro-2-naphthoic acid was also difficult.

Keene and Schofield\(^68\) obtained benzo(k)phenanthridone together with benzo(a)phenanthridone by a Schmidt reaction of 3,4-benzofluorenone with hydrazic acid. The separation of benzo(k)phenanthridone (86) from benzo(a)phenanthridone (87) was found to be difficult although they did effect the isolation of 86 and converted it, by Lithium Aluminium hydride reduction followed by dehydrogenation using Pd-C(30%), into the parent compound isolated as its picrate.
Kesavan, Devanathan and Arumugam have synthesised a few benzo(k)phenanthridines by proceeding through a Bruckner

\[ \text{HN}_3 \rightarrow \text{HN} \]

1. LiAlH\(_4\)

2. 30% Pd-\(\text{C} \)

\[ \text{R} = \text{H, CH}_3 \text{ etc;} \]
reaction of 1-(α-naphthyl)cyclohexene (38) with dinitrogen trioxide. The adduct was treated with a solution of sodium carbonate to give a nitrocyclohexyldinaphthalene (39) which on reduction (LiAlH₄), followed by acylation (RCOCl) and then cyclodehydration of the acyl compound with polyphosphoric acid gave hexahydrobenzo(k)phenanthridine 90. Dehydrogenation of 90 gave benzo(k)phenanthridine (6). The parent compound 6 (R = H₂) was obtained from the formamido compound by the two-step sequence outlined above. Multitudiness of the steps involved renders this method very disadvantageous. It also lacks generality.

Recently, a novel method has been reported from this laboratory for the synthesis of benzo(k)phenanthridine system. It is based on the AlCl₃-catalysed rearrangement of 4-phenyl-2,3-dihydrofuro(2,3-b)quinoline (91) which lead to 6-oxo-5,6,7,8-tetrahydrobenzo(k)phenanthridine (92) as depicted below.
The above rearrangement has been reported\textsuperscript{72} to proceed through a primary carbonium ion\textsuperscript{93} stabilized by the Tl-complex formation with the Tl-electron cloud of the C\textsubscript{4}-phenyl group which is in all probability orthogonal to the quinoline ring.
The required 4-phenyl-2,3-dihydrofuro(2,3-b)quinolines were prepared through the methods previously developed in this laboratory, one starting from 2-quinolone-3-acetic acid (94) and the other from 4-phenyl-3-vinylquinolones (7, R=Phenyl).
3-vinyl-2-quinolones (7) prepared from an o-amino carbonyl benzene and 3-butenoyl chloride by Shanmugam and co-workers, were earlier utilized in this laboratory for the synthesis of furan-6-10, thieno-11-14, selenolo-15,16 tellurolo-17 and pyrrolo(2,3-b)quinolines18(8).

\[ \text{R}^1 = \text{H, CH}_3, \text{C}_6\text{H}_5 \]
\[ \text{X} = \text{O, S, Se, Te & NH} \]

Among these vinylquinolines, the C-phenyl substituted ones bear the attractive possibility that they could be photolytically exploited involving the proximal phenyl and vinyl group to give benzo(k)phenanthridones as envisaged below. It was felt that if this expectation could be realized, it would indeed constitute a neat and elegant route to the benzo(k)phenanthridine ring system.
Before venturing into such a photochemical study one should profitably know where exactly the concerned molecule absorbs in its UV spectrum. The 2-oxo-4-phenyl-3-vinyl-1,2-dihydroquinoline (7) was chosen for the initial study. It showed its absorption maximum at $\lambda = 240$ nm. A solution of 7 in benzene (250 mg in 180 ml) was prepared and irradiated in a quartz vessel in Rayonet preparative photoreactor (see figure) using the 253.7 nm light. The starting material 7, slowly disappeared giving rise to a new compound as shown by Tlc. The photoreaction was almost complete within a period of six hours. The product showed absorption in its UV spectrum at 227 nm and it melted at 252 - 254°C. The nmr spectrum of the product documented the loss of the vinylic protons but showed instead a four proton singlet.
Photo- Reactor
The product was found to be identical with 6-oxo-5,6,7,8-tetrahydrobenzo(k)phenanthridine (92) (as shown by m.p., mixed m.p. superimposable IR, $^1$H nmr and elemental analysis) which was recently reported to result from the treatment of 4-phenyl-2,3-dihydrofuro(2,3-b)quinoline (91) with anhydrous aluminium chloride. Treatment of the photoproduct with phosphoryl chloride readily afforded a base identified to be 6-chloro-7,8-dihydrobenzo(k)phenanthridine (95) on the basis of its identity with the sample (m, p, mixed m.p., IR and nmr) previously prepared from 92 obtained from 91.
In another experiment, the 2-oxo-vinyl compound 7 was converted into 2-chloro-4-phenyl-3-vinylquinoline (96) by phosphoryl chloride-treatment and then photolyzed. The yield of the photoproduct viz., 95 was very appreciable and it required shorter duration than 7 for the completion of the cyclization reaction. Further, the chlorovinylquinolines, unlike the 2-oxo compounds are readily soluble in benzene.
Several non-oxidative photocyclizations similar to the above have been reported in the case of anilides,\textsuperscript{57} enamides,\textsuperscript{57} vinyl biphenyls\textsuperscript{27 - 31} though only to a limited extent in stilbene systems\textsuperscript{74} (Ref. Chapter I). Extension of the photocyclization reaction to the 4-phenyl-3-vinyl-2-quinolones \textsuperscript{7b} to \textsuperscript{7n} as well as to the 2-chloro-4-phenyl-3-vinylquinolines \textsuperscript{96b} to \textsuperscript{96n} led to the dihydrobenzo(k)-phenanthridines \textsuperscript{92b} to \textsuperscript{92n} and \textsuperscript{95b} to \textsuperscript{95n}. (Chart I and II) respectively.

In the irradiation of 2-chloro-4-phenyl-3-vinylquinoline (\textsuperscript{96}), even when no attempt (like purging with an inert gas, degassing etc.,) was made to exclude air, a single product only resulted. But in the photolysis of the vinylquinolone \textsuperscript{7}, the product \textsuperscript{92} was found to be contaminated with another one as revealed by the Tlc analysis. However, its formation could be prevented by purging the solution with nitrogen (for 15 minutes) before irradiation. We inferred that the formation of the minor product might be due to an oxidative photocyclization induced by the oxygen present in the non-degassed solution. To test our assumption, we carried out the photolysis in the presence of an oxidant viz., iodine. The reaction was monitored by Tlc and was found to be rather slow. The starting material slowly disappeared giving rise to a new product which in its Tlc appeared as a fluorescent spot. The photolysate, on work up, furnished a product in 54 \% yield which we presumed to be 6-\textsuperscript{oxo}-5,6-dihydrobenzo(k)-
phenanthridine (97). Its melting point corresponded to that of the authentic sample reported by Keene et al. 

Treatment of 97 with phosphoryl chloride furnished 99a m.p. 109 - 110°C (Literature m.p. 105 - 108°C). The structure assigned for the product was attested by the NMR spectrum, which showed all the protons in the aromatic region. An interesting observation in the nmr spectrum of 98 is the appearance of a low field two proton multiplet at $\delta = 8.66$ to 8.94, which are assigned to $C_1$ and $C_{12}$ protons. The assignments are similar to those established for $C_1$ and $C_{12}$ protons of benzo(c)phenanthrene (98). A further
discussion is deferred till the end of this chapter where the nmr spectra of various benzo(k)phenanthridines are dealt with.

The oxidative photocyclization was tried with the vinylquinolones 7b to 7l (chart I). In almost all cases a single photo product only was realized.

When the chloro compound 96a was subjected to oxidative photolysis (irradiation in the presence of iodine) it gave rise to a product Tlc of which showed two spots. The nmr spectrum indicated the product to be a mixture of the dihydrocompound 95 and the dehydrocompound 99a, in which however the dehydrocompound predominated. Even with higher concentrations of iodine, formation of the dihydrocompound prevailed.
However, when the oxidative photolysis was tried with the other 2-chloro-4-phenyl-3-vinylquinolines (96b to 96m) the formation of the dihydro compound was absent and only 6-chloro-benzo(k)phenanthridine was obtained exclusively. (chart II).
The photocyclization can be mechanistically viewed as follows.

\[ \text{Hydrogen abstraction} \]

\[ \text{Suprafacial (1,5)-Hydrogen shift} \]
Laarhoven, Horgan, Padwa, and Lapouyade have proposed that the photocyclization of structurally similar compounds occurs in two steps; a light induced cyclization of the hexatriene system followed by a thermally allowed suprafacial 1,5-hydrogen shift. Analogously cyclizes to generate an intermediate which undergoes electron demotion to ground state and subsequent suprafacial thermal 1,5-hydrogen shift, to give. The photochemically allowed antara shift is impossible here for steric reasons. Pornier de Violet et al. have recently adduced evidence for the intervention of an intermediate such as in the case of 1-(o-diphenyl)-1-phenyl ethylene (101) through laser flash photolysis.
In the oxidative photocyclization, the intermediate \( \text{100} \) suffers preferential hydrogen abstraction by the oxidant to give \( \text{99a} \) rather than undergo 1,5-hydrogenshift to give \( \text{95} \).

In the above photocyclization, the reactive species of the excited vinylquinoline may be a singlet or a triplet. With the view to ascertaining it, we carried out the photolysis of \( \text{7c} \) in the presence of oxygen, bubbled through the solution, which is known to be a triplet quencher.\(^8\) The ready formation of the photoproducts viz., \( \text{97c} \) and \( \text{92c} \) proved that the active species of the excited vinylquinoline is not a triplet but a singlet.

\[ \text{7c} \xrightarrow{h\gamma/O_2} \text{97c} + \text{92c} \]
An interesting observation is the ready occurrence of the photocyclization of 96o, even though it has a nitro group which has been reported, in the case of stilbenes, to inhibit the photocyclization.

Another interesting observation was encountered in the irradiation of 4-(2-substitutedphenyl)-3-vinylquinolines.
For example, when 2-chloro-6-methyl-4(2-chlorophenyl)-3-vinyl-quinoline (102) was irradiated under non-oxidative conditions, it gave rise to a product, which was found to be 99i and not the dihydrobenzo(k)phenanthridine 103 as shown by the following pieces of evidence.

![](https://example.com/structure.png)

1) The NMR spectrum showed the absence of methylene protons but instead showed a methyl singlet and nine protons in the aromatic region which correspond to the structure 99 (i).

2) Elemental analysis indicated the loss of elements of HCl in the product formation and corresponded to the formula (99i).

3) Mass spectrum also indicated the m/e to be 277 corresponding to the structure 99i and finally

4) The product was identical in all respects with the one derived from the oxidative photolysis of 96i.

In the formation of 99i from 102, the cyclization has occurred exclusively at the substituted in preference to the unsubstituted ortho position. The trihalocompound 104
likewise underwent eliminative photocyclization to give 2,6-dichlorobenzo(k)phenanthridine (99j)

A still more striking instance of photoelimination was observed in the case of the 2'-methoxy substituted vinylquinolines. When 2-chloro-4-(2,4-dimethoxyphenyl)-3-vinylquinoline (105) was irradiated, under exclusion of oxidants, it gave rise to two major products and they were separated by column chromatography. The fast moving component melted at 149° and its NMR spectrum revealed the presence of only one –OCH₃ group. It was presumed that its formation involved the loss of elements of methanol and the structure 99c thus assigned was further confirmed by elemental analysis,
mass spectrum and its identity with 6-chloro-10-methoxy-benzo-(k)phenanthridine (99c) derived from 96c by oxidative photolysis. The other component was identified to be 6-chloro-10,12-dimethoxy-7,8-dihydrobenzo(k)phenanthridine (106).
A similar eliminative photocyclization was observed in the case of 2-chloro-4-(2,5-dimethoxy phenyl)-3-vinylquinoline (107) which lead to 108 together with the dihydrocompound 109.

In the non-oxidative irradiation of 2,6-dichloro-4-(2-fluorophenyl)-3-vinylquinoline (107a) only product obtained was the corresponding dihydrocompound 95p and no defluorinated compound could be obtained.
In the case of the 2-oxo-4(2'-substituted phenyl)-3-vinylquinoline (110), \((x = \text{Cl or OMe})\) only the eliminative photocyclization exclusively occurred, leading to 97.

The mechanistic postulate for the photo elimination reaction observed in the case of 4-(2-substituted phenyl)-3-vinylquinolines like 102, 104, 105 and 107 is as follows.
The reaction is viewed as a hexatriene-cyclohexadiene ring closure to generate the intermediate 111 which then loses the elements of HX to form the benzo(k)phenanthridine system. The above mechanism is similar to the one proposed by Lenz and by Cava et al., in enamide photochemistry and Sargent et al. in Stilbene photochemistry.

Eliminative photo reactions involving ortho substitutents have been well documented in stilbene, azobenzene, anilide and enamide systems.

Stilbenes:

\[
\begin{align*}
\text{OCH}_3 & \quad \xrightarrow{\text{h}_\gamma} \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

Azobenzenes:

\[
\begin{align*}
\text{N} & \quad \xrightarrow{\text{h}_\gamma} \quad \text{CH}_4 \\
\end{align*}
\]
Anilides

Enamides

$X = \text{Cl, Br}$
Though there are several reports on the photolysis of 2,2'-divinyl biphenyls\textsuperscript{27, 28} and 2-vinyl biphenyls\textsuperscript{30, 31} ours appears to be the first instance wherein a vinyl group is involved in such eliminative photocyclizations.

Few reports have appeared in literature where in appropriately positioned methyl groups were found to undergo eliminative photolysis, but they occur, unlike in the case of -Cl, -OCH\textsubscript{3}, only under oxidative conditions.\textsuperscript{32, 82 - 85}

With the view to testing whether similar eliminative photolysis involving the methyl group can take place with 2-methyl substituted phenyl-3-vinyl-quinolines, we prepared the vinylquinolines 96f and 96g. (The required aminobenzophenonones 112 and 113 were also newly prepared) and photolysed them under oxidative and non-oxidative conditions.
96f as well as 96g gave, under both the conditions, a product that could result from non-eliminative as well as non-oxidative photocyclization. For example 96f gave only the dihydrocompound 95f under both the conditions.
More than its failure to undergo eliminative photolysis to give 99b, it's failure to undergo oxidative photolysis to give 114 was surprising. We presume that it may be due to the readiness of the photointermediate 115 to undergo 1,5-hydrogen shift to give 95f rather than subjecting itself to 'hydrogen abstraction' by the oxidant to give the dehydro-compound 114. The formation of 114 may not be energetically favourable perhaps due to the steric interaction...
of \( C_{12} \)-methyl with the peri(\( c_1 \)) position, which may be more pronounced with the fully aromatic compound 114 than with the dihydrocompound 25f where a certain amount of flexibility may be feasible.

Coming now to the various oxidative photoreactions carried out it is relevant to mention about the difficulty experienced in arriving at the optimum quantity of iodine to be used. With stilbenes, the amount of iodine used was very much less compared to that has been employed in the case of anilides. After much experimentation it was found that the use of 0.025 M of iodine was found to be sufficient to bring about the photocyclization of one mole of the substrate. With methoxy substituted compounds, however, the reaction could be brought about even with a lesser quantity of iodine.

Another noteworthy observation is that change of solvent from benzene to methanol improved the yield of the cyclized product appreciably in the case of vinylquinolines. This may be due to the vinylquinolone attaining an enhanced polarisation in the excited state which is stabilized by methanol - a polar solvent.
With 3',4'-disubstituted-4-phenyl-3-vinylquinolines, there is a possibility of obtaining two isomeric products depending upon the site of cyclization at the C4-phenyl ring. For example 96h can give either 116 or 95h or both on photocyclization. But 96h gave only 95h on non-oxidative photolysis and 99h on oxidative photolysis. The supporting evidence is that the nmr spectrum of 95h and as well as 99h exhibited a pair of singlets assignable to C9- and
C\textsubscript{12} protons. Similarly in 96e, the site of cyclization is the less hindered ortho position leading to 99e under oxidative conditions and 95e under non-oxidative conditions.

Having constructed benzo(k)phenantridine system in several varieties, we were then interested in obtaining the parent benzo(k)phenantridine, by a suitable technique either from the phenantridin-6(5H)one 97 or from the 6-chloro-benzo(k)phenantridine (99) and extend it to its derivatives.
Keene and Schofield have converted the phenanthridone 21 into the benzo(k)phenanthridine (6) by reduction with LiAlH₄ followed by dehydrogenation with Pd-C (30%). They as well as other workers have not reported on the conversion of the 6-chloro-phenanthridine into the parent phenanthridine.

\[ \text{i LiAlH}_4 \quad \text{ii Pd-C (30\%)} \]

The following methods were tried on 6-chloro-benzo(k)-phenanthridine with a view to effecting the hydrogenolysis of the 6-chloro group to give the parent benzo(k)phenanthridine.

1) Zinc/acetic acid:

Reduction with Zinc and acetic acid has been reported to be an effective reagent for the removal of chlorine in the C₂-position of quinoline, and related compounds. With the expectation to obtain 6 from 22, a solution of 22 in aqueous acetic acid was treated with Zinc at 70°C. But the product, on work up, was found to be the 6-oxo-compound (97). Apparently the chloro group has undergone solvolysis rather than hydrogenolysis.
ii) With hydrazine hydrate and CuSO₄:

Several 2- as well as 4- chloroquinolines have been converted into the dehaloquinolines by boiling with hydrazine hydrate and then treating the resulting hydrazino compound with cupric ions. A similar technique was tried on 99, but in our case, only the starting material was recovered.

iii) Catalytic hydrogenation (H₂)-Pd/C(10 %):

Catalytic hydrogenation in ethanol solution containing traces of KOH has been found to be fruitful in the conversion of 117 to 118 and other benzo(c) and benzo(a)-phenanthridines. (Recently Pinder has reviewed the reagents and methods that are available for the hydrogenolysis of organic halides). When a similar technique was attempted with 99, it readily afforded the benzo(k)phenanthridine in 80 % yield.
PA-C (10\%) 
(H_2)
Ethanol
KOH

99a → 6

99b → 6b

99l → 6b

99c → 6c + 133
The above hydrogenolysis technique was tried on a number of 6-chloro-benzo(k)phenanthridines and the results obtained are indicated in chart V. In all the cases the Tlc analysis showed, in addition to the spot corresponding to the major component, a fast moving one. The compound corresponding to the fast moving spot might be the 6-ethoxy derivative of the major component. In a few cases the 6-ethoxy compounds could be isolated and identified. With 99l, 99k and 99i interestingly, the halogen at the C_2-position was also found to undergo hydrogenolysis along with the chlorine at the C_6-position.

From the above investigation it has become evident that a productive sequence depicted below, for the synthesis of the parent benzo(k)phenanthidine is by way of 2-amino-5-chloro-(2-chloro)benzophenone (119) which is very easily accessible and via the photolysis of 104 which is neat and facile to give the phenanthidine 99i. Further, the
A clean transformation of 99i to give the parent benzo(k)-phenanthridine is also encouraging.
The Mass spectra of benzo(k)phenanthridines

The mass spectrum of benzo(k)phenanthridine (6) exhibited the parent peak as the base peak, at m/e = 229. However, 2-methyl benzo(k)phenanthridine (6e) showed the (P−1) peak (m/e = 242) as the base peak though the molecular ion peak (m/e = 243) was also present. Similar observations have been made with methyl substituted quinolines. It can be accounted for by the following fragmentation pattern.

\[ \text{H}_3\text{C} \quad \text{e}^- \quad \text{CH}_3 \]

\[ \text{M}^+; \text{m/e} = 243 \]

\[ \text{m/e} = 242 \]

However, in the case of the 10-methyl benzo(k)-phenanthridine (6b), the parent peak itself was the base peak.
Although benzo(k)phenanthridines are known for a long time, hitherto there is no report on the NMR spectra of these compounds. Despite the complexity of their spectra, which precluded complete assignment of all the signals, some protons are discernible from the rest.

All the five compounds investigated exhibited a singlet at δ 9.3 and this was assigned to C₆-H. The assignment is based on the following reasoning. (i) This singlet is absent in the corresponding 6-chloro benzo(k)-phenanthridines and (ii) similar observations have been reported for the C₆ - proton in benzo(a)- and benzo(c)-phenanthridines.
A low field multiplet at $\delta 8.90 - 9.25$ for $6a - 6c$ was assigned to $C_1^\text{-H}$ and $C_{12}^\text{-H}$. As reported earlier these hindered protons are deshielded by the ring current effect. In compound $6d$, while the $C_1^\text{-H}$ still appears as a low field multiple ($\delta 8.9 - 9.25$), the $C_{12}^\text{-H}$ gives a singlet ($\delta 8.58$). The significant (~0.4 ppm) upfield shift experienced by the $C_{12}^\text{-H}$ proton in $6d$ (as compared to $6a - 6c$) may be attributed to the electron releasing effect of the ortho and meta methoxyl groups. In $6e$, where an electron releasing methyl group is present in $C_2$-position the $C_1^\text{-H}$ shows an upfield shift and gives a doublet ($\delta 8.35, J = 2.5 \text{ Hz}$) and $C_{12}^\text{-H}$, a low field multiplet ($\delta 9.05 - 9.27$).

A multiplet, accounting for one proton, was observed at $\delta 8.20 - 8.45$ in compounds $6a - 6d$. Compound $6e$ however gave a one proton doublet at $\delta 8.2 (J = 9.0 \text{ Hz})$. This signal is assigned to $C_2^\text{-H}$. It was reported that in benzo(c)-phenanthrene, the $C_4^\text{-H}$ proton (and $C_9^\text{-H}$ proton) gives a multiplet centered at $\delta 7.95$. Thus the proximity of ring nitrogen to $C_4^\text{-H}$ in benzo(k)phenanthridine has resulted in a paramagnetic deshielding to the extent of 0.4 ppm. Similar, one proton, low field multiplet centered at $\delta 8.36$ was observed for $C_{11}^\text{-H}$ in benzo(c)acridine (XII).
A two proton singlet corresponding to C\textsubscript{7}-H and C\textsubscript{8}-H was observed at $\delta 7.88$ for all the five compounds. Similar A\textsubscript{2} pattern was reported$^{101}$ for the C\textsubscript{9}-H and C\textsubscript{10}-H in phenanthrene.

Thus in the NMR spectrum of benzo(k)phenanthridines $C_1$, $C_4$, $C_6$, $C_7$, and $C_8$ and $C_{12}$-protons could be assigned easily. However, the other proton signals could be assigned only when suitable substituents are present in nearby positions.
A COMPARISON OF THE NMR SPECTRA OF 6-CHLORO-BENZO(k)-PHENANTHRIDINES WITH THAT OF BENZO(c) PHENANTHRENES.

An analysis of the $^1H$ - NMR spectra of a number of 6-chloro-benzo(k)phenanthridines have been carried out. Ring distortion and electronic effects of substituents are fairly well reflected in the chemical shifts of these compounds. Also the spectra of 6-chlorobenzo(k)phenanthridines compare very well with those of benzo(c)phenanthrenes. It appears that the presence of a heteroatom in the ring at 5-position and a chlorine substituent at 6-position does not cause any appreciable perturbation of the $^1H$ resonance signals.

Fig. 1
Figure 1 compares the spectrum of 6-chloro-benzo(k)-phenanthridine with that of benzo(c)phenanthrene. The effect of the ring current and non-bonding interaction are reflected in the deshielding (~1 ppm) experienced by C\textsubscript{1}-H and C\textsubscript{12}-H in both the compounds.

\[ J_{2,3} = 5.4 \text{ Hz} \]

Figure 2 illustrates the effect of methoxy substituent at C\textsubscript{12}(also at C\textsubscript{10}) in benzo(k)phenanthridine and at C\textsubscript{1}-in benzo(c)phenanthrene on the spectra of these two compounds. The C\textsubscript{2}-H signal in benzo(c)phenanthrene and C\textsubscript{9}-H and C\textsubscript{11}-H signal in 6-chlorobenzo(k)phenanthridines are shifted upfield due to the electron releasing effect of the adjacent methoxy substituent. The signal at \( \delta \approx 6.92 \) in benzo(k)-phenanthridine is assigned to C\textsubscript{11}-H as this proton is
sandwiched between two methoxy substituents and hence feel the shielding effect of both of them. Methoxy substituents are known to shield ortho, meta and para protons in benzene ring system.\textsuperscript{96} The steric interaction of the substituent has probably twisted the ring system far out of planarity as to cause the disappearance of the unique downfield signal observed in compounds \textsuperscript{98} and \textsuperscript{99a}. Similar findings were reported\textsuperscript{95, 97} for 1-methyl benzo(c)phenanthrenes also.

![Chemical structures and spectra](image-url)
Figure 3 shows how the spectrum of 11-methoxy 6-chlor-benzo(k)phenanthridine compares with that of 2-methoxy benzo(c)phenanthrene. As could be seen the match is very good. A down field signal at δ 9.06 corresponding to C_1^-H in VI compares with the signal at δ 9.16 corresponding to C_{12}^-H in V. A doublet at δ 8.47 (J_{10,12} = 2.5 Hz) attributed to C_{12}^-H in VI matches with the doublet at δ 8.57 (J_{1,2} = 2.5 Hz) due to C_{1}^-H in V. The signal at δ 7.40 (dd, J_9 = 10 Hz, J_{10,12} = 2.5 Hz) corresponding to C_{10}^-H in VI compares favourably with a similar signal at δ 7.27 (d, d J_{3,4} = 8.6 Hz, J_{1,3} = 2.5 Hz) for C_3^-H in V. As in the previous cases, the methoxy substituent has caused an upfield shift (~0.4 pp of the adjacent proton signals. Except for the C_{4}^-H doublet at δ 8.27 (the downfield shift being attributed to the paramagnetic deshielding effect of the lone pair on nitrogen) the spectrum of VII appears similar to that of V. Again the electron releasing property of the methyl group is reflected in the upfield shift of the C_{3}^-H and C_{1}^-H signals. Also seen in fig. 3 is the effect of an electron withdrawing bromo substituent at the 2-position. The neighbouring proton signals are shifted downfield. C_{1}^-H appears as a doublet at δ 9.15 (J_{1,2} = 2.5 Hz). C_{4}^-H, also deshielded, appears as a doublet at δ 8.4 (J_{3,4} = 9 Hz).
Fig. 4 compares the spectra of compound IX & XI. The electron releasing methoxy substituent shields the neighbouring protons. Thus C_{9}-H and C_{11}-H in X and C_{2}-H and C_{4}-H in IX have their signals shifted upfield. As expected, in the bromo compound no such upfield shift was observed.
Discussion

Part-II
The 4-phenyl-3-vinylquinolines, prepared and used for the synthesis of the various benzo(k)phenantridines, were characterized by elemental (in the case of the new ones) as well as by spectral analysis.

Study of the N.M.R. spectra of the vinylquinolines revealed an interesting information on the preferred steric orientation of the vinyl with respect to the C2- and the C4-substituents and this forms the subject matter of this chapter.

In the case of the parent vinylquinolone (121)* the C4-methyl derivative 122 and 2-chloro-4-methyl-3-vinylquinoline (123), the vinylic protons give the expected AEX spectrum with the resonance for HA and HB falling in the range δ 5.2 - 6.4 and HX in the range of δ 6.65 - 7.25**

*Attempts to prepare the corresponding parent 2-chloro-3-vinylquinoline were not successful as reported earlier.

**back of computer facility and high resolution spectrometer precluded us from obtaining the actual values for the chemical shifts and coupling constants for the vinylic protons.
In the case of 4-phenyl-3-vinyl-2-quinolone (I), the pattern is found to be reversed and distorted. The $H_A$ and $H_B$ protons now absorb in the region $\delta 6.4 - 6.7$ and $H_X$ in the region $\delta 5.25 - 5.69$. **
But the pattern of the vinylic proton-absorption in the case of 2-chloro-4-phenyl-3-vinylquinoline (2i) is similar to those of the vinylquinolines 121 to 123.

$$H_{AB} = 6.4 - 6.7$$
$$H_X = 5.25 - 5.60$$

The same trend was noticeable in the case of the other 2-chloro-4-phenyl-3-vinylquinolines (96b - 96r) and a reversed and distorted version in the case of the corresponding 4-phenyl-3-vinylquinolones (7b - 7r). This indeed is perplexing.

A reasonable assumption which might explain this dichotomy is that in all these vinylquinolines the C4-phenyl
is orthogonal to the general molecular plane and the vinyl moiety assumes the "s-cis" conformation in the 2-chloro compounds and the "s-trans" conformation in the 2-oxo compounds.

That the 4-phenyl substituent exists in an orthogonal plane is indicated by the $C_5$-proton absorption in compounds 96m, 96n and 96k.
In compounds 124, 125 and 126, the C$_5$-H absorption occurs at a lower field (0.3 - 0.5 ppm) than in compounds 96m, 96n and 96k. The shielding experienced by the C$_5$-H proton in the latter compounds (95m, 96n and 96k) is apparently due to the diamagnetic anisotropy of the C$_4$-phenyl substituent. Model shows that if the phenyl substituent occupies an orthogonal plane, the C$_5$-H will fall in the shielding region of the phenyl ring. Such non-coplanarity of aryl rings in biaryls has been fairly well established by a number of workers in the past.

In compounds 95m, 95n and 95k, derived from 96m, 96n and 96k respectively, the C$_1$-H signal appears still at a lower field (0.2 - 0.4 ppm) than the C$_5$-H signal in compounds 124, 125 and 126. Being at the periphery of the aromatic ring system, the C$_1$-H in 95m, 95n and 95k experiences an additional diamagnetic deshielding due to the phenyl group which is more or less planar to the quinoline moiety.

In the vinylquinolines 96m, 96n and 96k it is not possible to exactly locate the C$_5$-proton signals since it forms part of the aromatic envelope. This may be due to the opposing effects of the two substituents i.e. the shielding effect of the orthogonal C$_4$-phenyl group and the deshielding effect of ortho substituents such as -NO$_2$, -Br and -Cl. However, when a -CH$_3$ group is present in the C$_4$-position, the C$_5$-proton is shielded both by the methyl and C$_4$-phenyl group and thus comes out of the aromatic envelope to be seen clearly as an unresolved doublet in the vinylquinoline 102 and the vinylquinolone 71 and 110a.
The conformation of the vinyl moiety can be either "cisoid" (127) or "transoid" (128). Any other conformation would be energetically unfavorable, as it would entail a loss of delocalization energy. The spectral data seem to indicate the predominance of a "cisoid" conformation for the vinyl moiety in 2-chloro-3-vinylquinolines and a "transoid" conformation for this residue in 2-oxo-3-vinylquinoline as illustrated above.

As mentioned earlier, in the 2-chloro-4-phenyl-3-vinylquinolines (where the normal ABX pattern was observed for the vinyl protons) the $H_A$ and $H_B$ proton signals appear at a
higher field than the Hx proton signal as the former would fall in the shielding region of the 4-phenyl substituent in the "cisoid" conformation (129). In the case of the oxo-compound, the Hx proton signal appears at a higher field than the HA and HB proton signals. This observation suggests the predominance of a "transoid" conformation (130) for these compounds since this would bring the Hx proton in the shielding region of the 4-phenyl ring.

![Image of structure 129]

The existence of the chloro compounds in the "cisoid" conformation may, probably, be due to van der Waal's repulsion between the 2-chloro substituent and H_B proton in the transoid conformation (130a). Scale models show considerable steric interaction between the 2-chloro substituent and H_B of the vinyl moiety. The predominance of "transoid" conformation in the case of 2-oxo-compounds is probably, partly due to reduced van
der Waal's interaction between the 2-oxo substituent and the \( H_B \) proton (the van der Waals radii of Oxygen is 1.4 Å as against 1.8 Å for chlorine; also \( C = O \) bond is shorter (1.23 Å) than \( C - Cl \) bond (1.7 Å))\(^3\) and partly due to the dipolar attraction\(^5\) between the positively polarized carbonyl carbon and the \( \pi \)-electron cloud of the vinyl moiety.

Results\(^6\) of photocyclization experiments further confirm the above conclusion. The chlorocompounds undergo cyclization faster (approximately twice) than the oxo compounds for the latter would require first a conformational isomerization from "transoid" to "cisoid" before they undergo cyclization.
The existence of the 4-phenyl substituent in an orthogonal plane in the 2-chloro-and 2-oxo-4-phenyl-3-vinylquinolines is further supported by the methyl proton resonance in compounds 96b, 96l, 96e-f, 7l, 7e-g.

Surveying the proton absorptions of the methyl at the various...
positions of the C₄-phenyl group, it is apparent that the C₂'-methyl protons appear at a higher field (δ 1.9 - 1.92), compared to the other methyl protons (δ 2.3° - 2.47). It can be reasonably assumed that the 2'-methyl group on the orthogonal phenyl ring protrudes into the shielding cone of the quinoline moiety.

An analogous situation exists with 2, 2', 6, 6'-tetramethyl biphenyl (131) where in the methyl groups were found to absorb at a higher field viz., δ 1.88. This was explained as being due to the shielding of each methyl group by the π-electrons of the distal ring, lying orthogonal to the ring bearing the methyl (the angle of torsion being 90°). In cases where there is deviation from orthogonality, the methyl group absorption shifts to a slightly lower value. For e.g., in 2,2'-dimethylbiphenyl (132), the methyl groups absorb at δ 2.03 (the angle of torsion was estimated to be 70°).
In the case of 2'-methyl-4-phenyl-3-vinylquinolines, the 2'-methyl absorbs at \( 1.9 \) which value is close to the value of 1.85 reported for the methyl group in compound 131. It is quite evident that in 4-phenyl-3-vinylquinolines, very much so in 2'-substituted-4-phenyl-3-vinylquinolines, the \( \text{C}_7 \) phenyl ring is orthogonal to the quinoline moiety with the angle of torsion 90° or nearly 90°.

With the cyclized products, also 'this methyl' experiences shielding but not so pronounced as in the case of its vinyl precursors. Here again, it can be assumed that the methyl comes slightly above the "A" ring resulting in a twisting of the "D" ring from the plane of the BC ring which would minimize its interaction with the \( \text{C}_1 \)-peri hydrogen. Such a twisting is also reflected in the absorption of the \( \text{C}_8 - \text{C}_9 \) methylene proton which appears as an ill-defined multiplet rather than an unresolved singlet which has been the case with the dihydrobenzo(k)phenanthridines lacking a \( \text{C}_{12} \)-methyl substituent. In this context it is pertinent to mention here that X-ray evidence has confirmed that in benzo(c)-phenanthrene the "A" ring and "D" ring are twisted in opposite directions in order to minimize the \( \text{C}_1 \)-H and \( \text{C}_{12} \)-H interaction.