

**FLUORESCENCE AND TRIPLET YIELD QUENCHING OF  $\beta$ -APO-14'-CAROTENAL ( $C_{22}$  ALDEHYDE) BY AROMATIC MOLECULES**N. SELVARAJAN<sup>†</sup>, P. K. DAS and G. L. HUG*Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)*

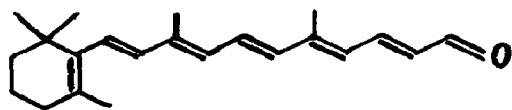
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**Summary**

The fluorescence and triplet yields of  $\beta$ -apo-14'-carotenal in cyclohexane at room temperature are quenched in the presence of submolar concentrations of aromatic molecules predominantly through a dynamic interaction. The observed Stern-Volmer constants  $K_{SV}^F$  for fluorescence quenching vary from  $0.06 M^{-1}$  for mesitylene to  $45 M^{-1}$  for indole, giving excited state quenching rate constants in the range  $6 \times 10^7 - 4.5 \times 10^{10} M^{-1} s^{-1}$ . With methoxy-substituted benzene derivatives as quenchers, the  $K_{SV}^F$  data correlate well with the half-wave oxidation potentials of the quenchers, suggesting a modest involvement of charge transfer. Interestingly, the Stern-Volmer constants  $K_{SV}^T$  for triplet yield quenching are significantly higher than the corresponding  $K_{SV}^F$  values. This result is explained in terms of scheme(s) where the singlet excited state species that acts as precursor for triplet is assumed to be kinetically distinguishable from that responsible for fluorescence.

**1. Introduction**

Among retinal-related polyenals of varying chain lengths,  $\beta$ -apo-14'-carotenal ( $C_{22}$  aldehyde) (Fig. 1), the immediately higher homologue of

Fig. 1.  $C_{22}$  aldehyde.<sup>†</sup> Deceased.

retinal, is unique [1 - 3] in that under certain conditions it displays both significant room temperature fluorescence and significant quantum yields of triplet formation. For example it has pronounced fluorescence ( $\phi_F \approx 0.01$  in 3-methylpentane) as well as high quantum yields of lowest triplet occupation ( $\phi_T \approx 0.5$  in cyclohexane) at room temperature in non-polar aliphatic hydrocarbon solvents. Both  $\phi_F$  and  $\phi_T$  of this long-chain polyenal are strongly dependent [1, 2] on the nature of the solvent, however, and as a general rule undergo significant reduction on changing from a non-polar solvent to a polar and/or a hydrogen bonding solvent. The object of the present study is an exception to this rule. This exception is for the case of benzene as a solvent where  $\phi_T$  of  $C_{22}$  aldehyde is significantly lower than might be expected from a comparison with other non-polar solvents such as 3-methylpentane or cyclohexane. In this respect  $C_{22}$  aldehyde differs from retinal and its immediately lower homologue ( $C_{17}$  aldehyde). The  $\phi_T$  values of retinal and  $C_{17}$  aldehyde are also quite high, but they are of comparable magnitudes (0.4 - 0.7) in both benzene and hydrocarbon solvents (aliphatic).

In this paper we have addressed the question of whether the large decrease (more than 14-fold) in the  $\phi_T$  of  $C_{22}$  aldehyde on going from 3-methylpentane to benzene could arise from a specific interaction of the lowest excited singlet state of the polyenal with the aromatic system rather than from an environmentally induced change in the state order. Based on spectral and photophysical data and on considerations of state orders in related polyene systems, the lowest excited singlet state of  $C_{22}$  aldehyde has been assigned [1] a  $(\pi, \pi^*)$  character which is probably  ${}^1A_g^{*-}$  like. In the usual kinetic scheme of competing first-order processes large  $\phi_T$  values in non-polar solvents can then be explained in terms of a lower lying  ${}^3(n, \pi^*)$  state and a contribution of the favorable  ${}^1(\pi, \pi^*) \rightarrow {}^3(n, \pi^*)$  process to the intersystem crossing. At the same time, small  $\phi_T$  values in the polar and/or hydrogen bonding solvents can be attributed to a reversal of the state order involving the lowest  ${}^1(\pi, \pi^*)$  and  ${}^3(n, \pi^*)$  states induced by the solvent effect and/or specific hydrogen bonding. This model, however, cannot explain why benzene is as efficient as acetonitrile (or methanol) in lowering the  $\phi_T$  of  $C_{22}$  aldehyde. More importantly, as the present study will show,  $\phi_F$  of  $C_{22}$  aldehyde also decreases considerably on going from cyclohexane to benzene suggesting that the interaction in benzene results in enhancement of pathway(s) that are in competition with those representing fluorescence and intersystem crossing and hence there is a simultaneous decrease in the yields of both the latter processes.

We have examined how the presence of submolar quantities of benzene and of a series of methyl- and methoxy-substituted benzene derivatives as quenchers in cyclohexane solutions of  $C_{22}$  aldehyde at room temperature affects the fluorescence intensity and in some cases the triplet yield of the polyenal. The results should be of interest in understanding the possible role of the excited state interaction, if any, between the retinyl moiety and aromatic residues of proteins in such photobiological systems as rhodopsin (visual pigment) and bacteriorhodopsin. To the best of our knowledge,

although there have been many studies concerning singlet exciplex interactions between aromatic molecules and olefins or polyenes of short chain length, namely dienes [4 - 6], styrenes and stilbenes [7] and diphenylbutadiene [8], so far no attention has been paid to the behavior of long-chain polyene systems in this respect.

## 2. Experimental details

C<sub>22</sub> aldehyde was synthesized from all-*trans* retinal (Eastman) by the procedure described in a previous paper [9]. The crude polyenal was chromatographed on a silica gel column using petroleum ether-10% diethyl ether as the eluent and was then crystallized as deep red needles from *n*-hexane. The sources, syntheses and purification of the methoxy-substituted benzene derivatives have been reported elsewhere [10]. The methylated benzenes, all obtained from Aldrich, were purified either by fractional distillation or recrystallization (from benzene or benzene-ethanol mixtures). Benzene (Aldrich) and cyclohexane (MC/B), both of spectral grade, were used without further purification.

Practically all of the fluorescence spectral measurements were carried out in square quartz cells of dimensions 1 cm × 1 cm using a Spex Fluorolog photon counting spectrofluorometer with a 90° configuration between excitation and observation of emission. Some measurements, mostly confirmatory, were performed using an SLM photon counting apparatus, the description of which is given elsewhere [11]. Since there was practically no difference between the fluorescence intensities (or triplet yields) in degassed and non-degassed solutions, non-degassed C<sub>22</sub> aldehyde solutions in cyclohexane were used for fluorescence quenching studies.

The laser flash photolysis apparatus used for the measurement of relative triplet yields is described elsewhere [10 - 12]. Nitrogen laser pulses (337.1 nm; 8 ns; 2 - 3 mJ) from a Molelectron UV-400 system were used for excitation. The triplet of C<sub>22</sub> aldehyde was monitored by its spectral absorption at 470 - 480 nm using solutions that were degassed by bubbling argon. Front face laser excitation in quartz cells of dimensions 1 cm × 0.2 cm with optically flat surfaces was used with the monitoring light (pulsed 450 W xenon lamp) meeting the laser beam at an angle of about 20° in the cell along its 0.2 cm path length.

## 3. Results

The room temperature fluorescence spectra of C<sub>22</sub> aldehyde obtained from optically matched solutions in cyclohexane and benzene are shown in Fig. 2, curves A and B. The spectra are very similar in shape and location in the two solvents ( $\lambda_{\max} = 620$  nm, uncorrected for detector response). There is about a ninefold decrease in fluorescence intensity on going from cyclo-

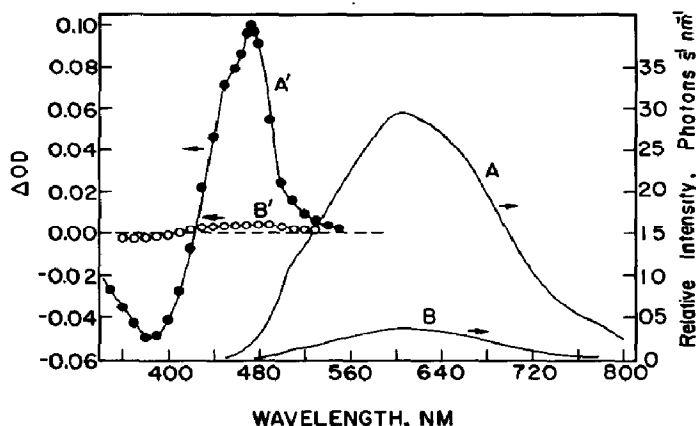


Fig. 2. Fluorescence spectra (curves A and B) and T-T absorption spectra (curves A' and B') of  $C_{22}$  aldehyde (about  $10^{-5}$  M) obtained from optically matched solutions in cyclohexane (curves A and A') and benzene (curves B and B'). The fluorescence spectra were obtained by excitation at 420 nm in the Fluorolog spectrofluorometer and are not corrected for detector sensitivity. The T-T spectra were obtained by pulsed excitation at 337.1 nm (nitrogen laser).

hexane to benzene, however. Figure 2, curves A' and B', shows the triplet-triplet (T-T) absorption spectra of  $C_{22}$  aldehyde in the two solvents obtained by direct laser excitation of optically matched solutions (optical density of 0.07 at 337.1 nm in a 3 mm cell). A comparison of the absorbances at the wavelength maxima (473 nm in cyclohexane and 485 nm in benzene) shows that the triplet yield in benzene is about a factor of 20 less than that in cyclohexane (assuming a similar maximum extinction coefficient for T-T absorption in the two solvents).

The quenching effects of various aromatic molecules on the fluorescence and the triplet yield of  $C_{22}$  aldehyde are expressed in terms of the observed Stern-Volmer constants  $K_{SV}^F$  and  $K_{SV}^T$  using plots based on the equations

$$\frac{\phi_{F,0}}{\phi_F} = 1 + K_{SV}^F [Q] \quad (1)$$

$$\frac{\phi_{T,0}}{\phi_T} = 1 + K_{SV}^T [Q] \quad (2)$$

where  $\phi_F$  and  $\phi_T$  are the fluorescence yield and the triplet yield respectively at the quencher concentration  $[Q]$ , and  $\phi_{F,0}$  and  $\phi_{T,0}$  are the corresponding yields in the absence of the quencher. The plots of  $\phi_{F,0}/\phi_F$  and  $\phi_{T,0}/\phi_T$  against  $[Q]$  were approximately linear except in the case of benzonitrile. Some typical plots are shown in Fig. 3. The  $K_{SV}^F$  and  $K_{SV}^T$  values and the maximum quencher concentrations used to determine them are given in Tables 1 and 2.

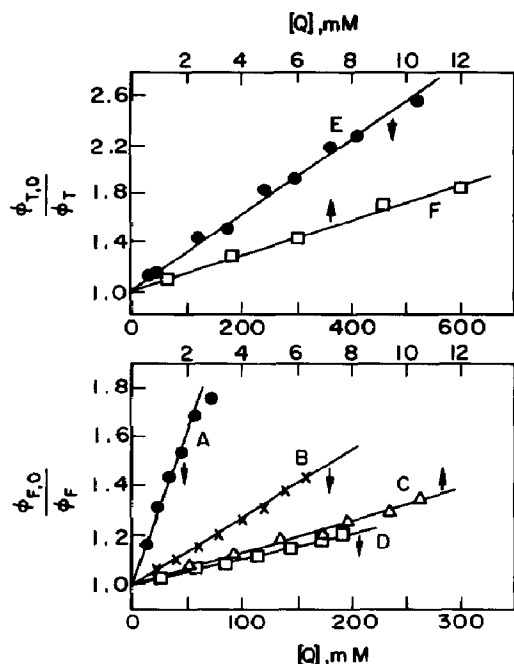


Fig. 3. Stern-Volmer plots for fluorescence (curves A - D) and triplet yield (curves E and F) quenching of  $C_{22}$  aldehyde in cyclohexane by 3,5-dimethoxy-*N,N*-dimethylaniline (curve A), 1,2,4-trimethoxybenzene (curves B and E), indole (curves C and F) and 1,3,5-trimethoxybenzene (curve D).

TABLE 1

Stern-Volmer constants for the fluorescence quenching of  $C_{22}$  aldehyde by aromatic molecules in cyclohexane

Quencher	Maximum concentration used (M)	$K_{SV}^{F^a}$ ( $M^{-1}$ )
Benzene (1)	0.70	0.3
Toluene (2)	0.25	1.2
<i>p</i> -xylene (3)	0.50	0.3
Mesitylene (4)	0.60	$\approx 0.06$
Durene (5)	0.15	2.2
Pentamethylbenzene (6)	0.15	2.7
Hexamethylbenzene (7)	0.13	2.9
Benzonitrile (8)	0.10	2.4
Indole (9)	0.01	45
Anisole (10)	0.40	0.4
1,2-dimethoxybenzene (11)	0.40	1.4
1,3-dimethoxybenzene (12)	0.4	1.5
1,4-dimethoxybenzene (13)	0.20	1.5
1,2,3-trimethoxybenzene (14)	0.25	1.0
1,2,4-trimethoxybenzene (15)	0.30	2.4
1,3,5-trimethoxybenzene (16)	0.20	1.0
3,5-dimethoxy- <i>N,N</i> -dimethylaniline (17)	0.05	12
<i>p</i> -methoxy- <i>N,N</i> -dimethylaniline (18)	0.05	18

<sup>a</sup> Estimated range of error,  $\pm 15\%$ .

TABLE 2

Stern-Volmer constants for triplet yield quenching of C<sub>22</sub> aldehyde in cyclohexane

Quencher	Maximum concentration used (M)	K <sub>SV</sub> <sup>T a</sup> (M <sup>-1</sup> )
Benzene	0.75	0.6
Naphthalene	0.6	1.4
Benzonitrile	0.5	5.3
1,2,4-trimethoxybenzene	0.5	3.2
Indole	0.012	71
1,4-dimethoxybenzene	0.3	2.7

<sup>a</sup>Estimated range of error, ±25%.

Among the quenchers listed in Tables 1 and 2, benzonitrile and to some extent indole are found to form ground state complexes with C<sub>22</sub> aldehyde in the concentration range used for quenching measurements. This is shown by a slight enhancement of ground state spectral absorption in the long wavelength tail (450 - 490 nm) as well as by the concomitant lowering of the absorption intensity near the wavelength maximum (380 - 410 nm). The isosbestic points are at 430 nm and 445 nm for indole and benzonitrile respectively. Fluorescence quenching studies for these two quenchers were carried out using excitation at the isosbestic points so that the total absorbance and hence the intensity of the exciting light absorbed in the volume of the solution that was monitored for emission were constant at varying [Q] values. Also, at the laser excitation wavelength (337.1 nm) used for studies of the lowering of the triplet yield the absorbance change as a function of benzonitrile or indole concentration was too small to be taken into account.

When quenching occurs because of both ground state (static) and excited state (dynamic) interactions, supralinear behavior is expected in the Stern-Volmer plots. Such a situation seems to have been realized in the case of benzonitrile as the quencher. The plots of  $\phi_{F,0}/\phi_F$  and  $\phi_{T,0}/\phi_T$  versus the benzonitrile concentration are distinctly bent upwards (see Fig. 4, curves A and B respectively). When a model based on the formation of a non-fluorescing ground state complex



is used and it is assumed that in the excited state the complex does not decompose into the free form (excited state), *i.e.* the excited state quenching process represented by



is essentially irreversible, we obtain the following equation for fluorescence quenching with excitation at the isosbestic point:

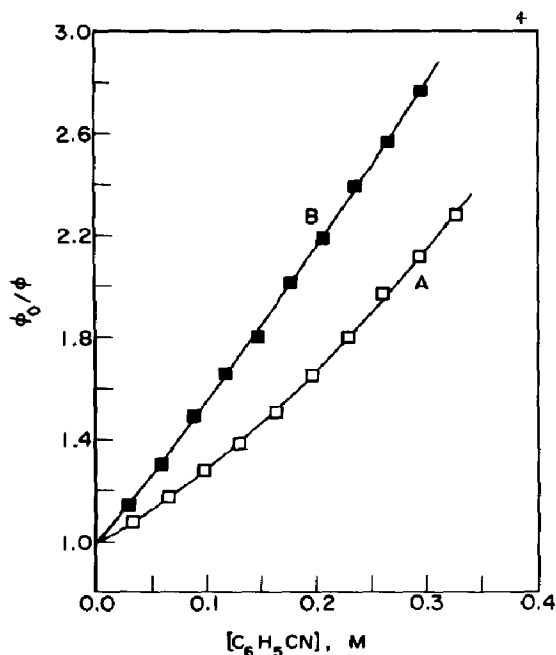


Fig. 4. Stern-Volmer plot for the quenching of the fluorescence (curve A) and the triplet yield (curve B) of  $C_{22}$  aldehyde in cyclohexane by benzonitrile: —, calculated curves. The least-squares best fit of the data to expressions quadratic in  $[Q]$  gives  $\phi_{F,0}/\phi_F = 0.995 + 2.40[Q] + 4.77[Q]^2$  and  $\phi_{T,0}/\phi_T = 0.992 + 5.28[Q] + 2.63[Q]^2$ .

$$\frac{\phi_{F,0}}{\phi_F} = (1 + K_G[Q])(1 + K_{SV}^F[Q]) \quad (5)$$

where  $K_G$  is the equilibrium constant for the formation of the ground state complex (eqn. (3)) and is given by

$$K_G^{-1} = \frac{[A][Q]}{[A \dots Q]} \quad (6)$$

An analogous quadratic (supralinear) dependence of  $\phi_{T,0}/\phi_T$  on  $[Q]$  should be observed, provided that the complex  $A \dots Q$  has zero (or low) triplet yield. A least-squares best fit of the data in Fig. 4, curves A and B, to polynomials quadratic in  $[Q]$  gives  $2.4 \text{ M}^{-1}$  and  $5.3 \text{ M}^{-1}$  for  $K_{SV}^F + K_G$  and  $K_{SV}^T + K_G$  respectively.

Although the absorption spectrum of  $C_{22}$  aldehyde in the presence of indole suggests the formation of a ground state complex, presumably through hydrogen bonding, the Stern-Volmer plots for triplet yield or fluorescence quenching do not show any significant deviation from linearity (Fig. 3, curves C and F). This is explainable by the fact that in this case  $K_{SV}$  dominates  $K_G$ .

We have used some typical quenchers which interact with  $C_{22}$  aldehyde relatively strongly, *i.e.* 1,2,4-trimethoxybenzene, benzonitrile and indole, to

examine in detail whether distinct emissions or T-T absorptions attributable to exciplexes could be observed. Both fluorescence and T-T absorption spectra in the presence of the highest concentrations of quencher are found to be similar in shape and location to those observed for the polyenal in the absence of a quencher. In view of the fact that the sensitivity of the detection system (EMI 9635QA photomultiplier tube) in our fluorometric set-up was relatively small in the long wavelength region (above 600 nm), our inability to detect a change in the fluorescence spectra is taken to mean that the exciplex emission, if any, is weak and does not contribute significantly in the spectral region (510 - 550 nm) where the fluorescence was monitored for the quenching studies.

With 1,2,4-trimethoxybenzene as the quencher, the variation in  $K_{SV}^F$  with respect to the excitation wavelength (340 - 440 nm), the monitoring wavelength (500 - 600 nm) and the  $C_{22}$  aldehyde concentration ( $3 \times 10^{-6}$  -  $2 \times 10^{-5}$  M) was examined. We obtained  $K_{SV}^F$  values within  $\pm 0.3 M^{-1}$  of a mean value of  $2.4 M^{-1}$ . Combined with the facts that there is practically no dependence of the excitation spectra of  $C_{22}$  aldehyde on fluorescence monitoring wavelengths and that both the fluorescence spectra and the yields are changed only slightly when the excitation wavelengths are changed [1], the observed invariance of  $K_{SV}^F$  suggests that it corresponds to a well-defined fluorescing species formed after excitation and relaxation in the singlet manifold.

#### 4. Discussion

The results presented in Section 3 suggest that the observed quenching of the fluorescence and the triplet yield of  $C_{22}$  aldehyde can arise from static and/or dynamic interactions. That both interactions are possible is established by the case of benzonitrile where evidence is obtained from both changes in the ground state absorption spectra and the supralinear behavior of Stern-Volmer plots. In the other cases the plots do not bend, suggesting that one form of interaction dominates over the other; furthermore, except with indole, no change in the ground state absorption spectra is observed in the presence of the quenchers. It appears highly unlikely that, with quenchers other than indole and benzonitrile, ground state complexes with absorption identical with that of the free polyenal are formed. On this basis we argue that the quenching observed in these cases is predominantly a result of dynamic interactions. The preliminary results of our measurements of the fluorescence lifetime  $\tau_F$  (based on the time-correlated photon counting technique using equipment from Photochemical Research Associates with a hydrogen-filled thyratron-operated spark lamp) do indicate a shortening of the measured lifetime in the presence of a quencher (1,2,4-trimethoxybenzene), suggesting the involvement of excited state interaction.

The reported room temperature lifetime  $\tau_F$  of  $C_{22}$  aldehyde fluorescence is 0.8 ns in 3-methylpentane [1]. If  $\tau_F$  is assumed to be similar (*i.e.*



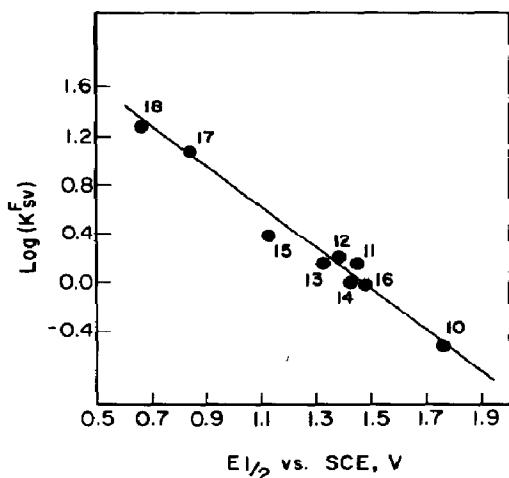


Fig. 5. Plot of  $\log K_{SV}^F$  against the half-wave oxidation potential of methoxybenzenes. The numbering of the quenchers is given in Table 1. The  $E_{1/2}$  values were taken from ref. 13. The straight line for the least-squares best fit (unweighted) is given by  $\log K_{SV}^F = -1.53(E_{1/2}) + 2.26$  where  $K_{SV}^F$  is in reciprocal moles per liter and  $E_{1/2}$  is in volts against a standard calomel electrode.

about 1 ns) in cyclohexane, the  $K_{SV}^F$  data in Table 2 give, for bimolecular quenching rate constants, values in the range  $6 \times 10^7 - 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . However, this is based on the simple kinetic model of competing first-order processes originating from the lowest singlet state of the polyenal. As will be seen shortly, the situation is probably more complicated.

In the literature [4 - 7] singlet quenching is often associated with a mechanism where an exciplex is formed between the quencher and the fluorophore. In the present study no new emission due to a singlet exciplex could be observed. While the intermediacy of an exciplex is not established, the role of charge transfer in the quenching interaction is quite evident. That charge transfer is possible both from and to the polyenal is demonstrated by the fact that benzonitrile (an acceptor) is as good a quencher as 1,2,4-trimethoxybenzene (a donor) in terms of the  $K_{SV}^F$  value. A plot of  $\log K_{SV}^F$  against the half-wave oxidation potentials of the methoxy-substituted benzene derivatives is shown in Fig. 5. The observed linearity with slope  $-1.5 \text{ V}^{-1}$  suggests that excited state charge transfer interaction is operative to a modest extent in the quenching mechanism.

A comment is in order regarding indole, the most effective quencher in Tables 1 and 2. A separate study [14] using alcohols as quenchers has shown that a specific hydrogen bonding interaction in both the ground and excited states of  $C_{22}$  aldehyde results in a dramatic quenching of both the fluorescence intensity and the triplet yield. Obviously, such a hydrogen bonding effect is also present in the case of indole and can contribute significantly to  $K_{SV}^F$  or  $K_{SV}^T$ .

Perhaps the most interesting finding in the present study is that for the quenchers for which both  $K_{SV}^F$  and  $K_{SV}^T$  data are available (see Tables 1 and

2),  $K_{SV}^F$  is invariably smaller than  $K_{SV}^T$ . In most cases the discrepancy is beyond the estimated range of errors. A similar discrepancy, but more pronounced, has also been observed during a study of quenching by hydrogen bonding agents, *e.g.* alcohols [14]. These results clearly suggest that the singlet excited state species responsible for fluorescence is different from the species that acts as the predominant precursor for the triplet. In the light of this we first consider the following scheme where the initially formed singlet excited state  $^1A^*$  (fluorescing) goes through a second excited state  $^1B^*$  (non-fluorescing) in order to make a transition by intersystem crossing to the triplet manifold (analogous schemes have in fact been invoked by various workers to explain the photophysics of diphenylpolyenes [15, 16]):



One possible identification of B can be a twisted form (conformer) of the polyenal. If steady state approximations for [ $^1A^*$ ] and [ $^1B^*$ ] (for fluorescence measurements) are used and the differential equations concerning the transient behavior of  $A^*$  and  $B^*$  following pulsed laser excitation (for triplet yield measurements) are solved, it is possible to express  $\phi_{F,0}/\phi_F$  and  $\phi_{T,0}/\phi_T$  as functions of [Q]. Such treatments give the following result:

$$\chi_{SV}^T = \chi_{SV}^F + \frac{k_4}{k_{-3} + k_5} \quad (7)$$

where  $\chi_{SV}^F$  and  $\chi_{SV}^T$  are the coefficients of the terms linear in [Q] in the expressions for  $\phi_{F,0}/\phi_F$  and  $\phi_{T,0}/\phi_T$  respectively. Since in our measurements  $\chi_{SV}^F \approx K_{SV}^F$  and  $\chi_{SV}^T \approx K_{SV}^T$ , the observation that  $K_{SV}^T$  is greater than  $K_{SV}^F$  becomes explainable. However, the serious problem with the above scheme is that it predicts a sublinear behavior for fluorescence quenching and a supralinear behavior for triplet yield quenching. While the former disappears for  $k_{-3} \ll k_3$ , *i.e.* if step (III) is essentially irreversible, the latter behavior should still be observable for triplet yield quenching (because of the two-step quenching represented by steps (II) and (IV)). Within the accuracy of our measurements and in the concentration ranges used for [Q] we have been unable to detect any significant well-defined non-linearity in the quenching plots (except for benzonitrile).

Another possibility is that a distribution of non-interconvertible singlet excited states corresponding to various conformeric species is attained under thermal equilibration following excitation and relaxation; these species become responsible, rather independently, for fluorescence, internal conversion and intersystem crossing. Such a model can explain why  $K_{SV}^T$  is different from  $K_{SV}^F$  and also why deviation from linearity is not observed for Stern-Volmer quenching plots. As a matter of fact, on the basis of picosecond studies Hochstrasser *et al.* [17] have proposed a similar "tree" model to explain the room temperature photophysics of all-*trans* retinal (immediate lower homologue of C<sub>22</sub> aldehyde) for which the decay of singlet-singlet absorption (in *n*-hexane) is found to occur with a time constant (20 ps) smaller than that observed for the growth of T-T absorption (34 ps). A similar study concerning transient phenomena of C<sub>22</sub> aldehyde on a subnanosecond time scale would be of interest for throwing more light on some of the issues addressed in the present work.

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