exception to this Hirayama rule ($n = 3$) published to date is the 1,4-di-(1-naphthyl) butane, where a weak emission ascribed to an intramolecular excimer was observed, but only at low temperatures (Chandross and Dempster [2]). Studies of dinaphthyl-propane [2] and of bicarbazolylpropane [3 - 5] essentially confirmed the generality of the $n = 3$ rule.

In order to clarify the factors governing the generality of the Hirayama rule, the fluorescence of a series of α, ω-di-(3-pyrenyl)-alkanes, $Py(CH_2)_n Py$, with $n = 2,...,16$ and 22 was studied. It was felt that the steric and statistical reasons which have been invoked to explain the Hirayama rule could be less important than the magnitude of the stabilization energy of the intramolecular excimer. Pyrene was chosen because of its large excimer stabilization energy. For $Py-(CH_2)_n-Py$, in methylcyclohexane(MCH) solution ($1.0 \times 10^{-5}M$) at room temperature, intramolecular excimer emission was observed for all dipyrenylalkanes investigated, except for $n = 7$. Thus in contrast to the systems previously investigated, excimer fluorescence is clearly not restricted to the case where $n = 3$.

The intensity of excimer emission shows a minimum for $n = 7, 8$, in a pattern reminiscent of *i.a.* the cyclization yield of ω-oxy acids as a function of chain length, as reported by Stoll and Rouvé in 1935, see [6].

In the series of α,ω-di-(3-pyrenyl)al-kanes a variation of the energy of the excimer emission maximum with the length of the CH_2-chain is observed.

An investigation of the time dependence of the monomer and excimer fluorescence after pulse excitation (N_2-laser), reveals *i.a.* a non-exponential decay when the monomer fluorescence of *e.g.* $Py-(CH_2)_4Py$ and $Py(CH_2)_9Py$ is studied at the zero-zero transition at room temperature. This behaviour can be explained by assuming that the repopulation of the monomer from the initially formed excimer is an important process for $Py(4)Py$ and $Py(9)$ Py at room temperature. For 1,3-di-(9-phenanthryl)propane, $Phen(CH_2)_3Phen$, an emission from an intramolecular excimer could not be observed over a large temperature range, in contrast to $Phen-(C=O)-(CH_2)_2-Phen$ where a new emis-

sion at longer wavelength could in fact be measured.

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O3
Photophysics of diphenylpolyenes

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Observations have been made of the fluorescence lifetime (τ) and quantum yield (ϕ_F) of the first four all-*trans* diphenylpolyenes (*trans*-stilbene, diphenyl-butadiene, diphenylhexatriene and diphenyloctatetraene) in seven solvents from -50 to 50 °C.

The radiative lifetime τ_F ($= \tau/\phi_F$) exhibits several anomalies.

1. τ_F exceeds the theoretical radiative lifetime τ_A calculated from the integrated absorption spectrum.
2. τ_F/τ_A increases with the polyene chain length.
3. τ_F/τ_A increases with the degree of departure from mirror symmetry between the fluorescence and absorption spectra.
4. τ_F/τ_A increases with the Stokes shift between the absorption and fluorescence maxima.
5. τ_F depends markedly on the solvent.
6. τ_F increases with increase in temperature.

Similar anomalies occur in the retinol polyenes.

The following model is proposed to account for the behaviour. A polyene has a ^1A_g ground state and ^1B_u and $^1A_g(^1A_g*)$ excited states which are adjacent. After Franck-Condon excitation of the all-*trans* configuration ($\theta = 0°$) by the allowed $^1B_u \leftarrow ^1A_g$ absorption transition, molecular relaxation occurs. The phenyl groups rotate through a relative angle θ about the

polyene chain, causing the departure from mirror symmetry, an increased Stokes shift, and in the extreme case ($\theta = 180°$) *trans–cis* isomerization. The increase in θ reduces the $^1A_g{}^*$ energy and increases the ^1B_u energy, so that when θ exceeds a critical value θ_c ($\geqslant 0$) the $^1B_u - {}^1A_g{}^*$ energy gap ΔE becomes positive and increases with θ. The fluorescence then corresponds to the forbidden $^1A_g \rightarrow {}^1A_g$ transition (rate k_F) which derives its oscillator strength by coupling to the allowed $^1B_u \rightarrow {}^1A_g$ transition (rate k_A) so that

$$k_F = K^2 k_A / \Delta E^2$$

corresponding to

$$\tau_F / \tau_A = \Delta E^2 / K^2$$

where K is the matrix element coupling the two transitions. τ_F and τ_F / τ_A thus depend on ΔE and θ, which are influenced by the solvent, temperature and polyene chain length. The intramolecular radiationless transitions (intersystem crossing, internal conversion, *trans–cis* isomerization) also depend on θ, and they are subject to similar solvent and temperature effects.

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O6
Formation of the Excited Triplet, the Excited Singlet and the Excimer of Octafluoronaphthalene in Solution

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The octafluoronaphthalene (OFN) excited triplet is formed by flash photolysis of OFN solutions in methylcyclohexane, acetonitrile, benzene and carbon tetrachloride. Formation of the triplet is photosensitized by phenanthrene and decafluorobenzophenone. The OFN triplet is also formed by pulse radiolysis of solutions of OFN in benzene and methylcyclohexane.

Emission from dilute solutions ($10^{-4} - 10^{-3}$ M) of OFN in benzene and methylcyclohexane has been observed by photoexcitation and pulse radiolysis. The emission λ_{max} is at ~ 350 nm, in reasonable agreement with previously published data

and is attributed to the OFN excited singlet.

The emission λ_{max} shifts slowly towards the red as the OFN concentration is increased, in both photoexcitation and pulse radiolysis studies. The magnitude of the shift is small (~ 10 nm). The emission spectra obtained at 10^{-4} M OFN in solutions in benzene and methylcyclohexane are attributed to the OFN excimer.

O9
Direct Determination of the Triplet Quantum Yields of Acridine in Polar and Non-Polar Solvents

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The present work reports direct measurement of $S \rightarrow T$ intersystem crossing (ISC) quantum yield of acridine (the heterocyclic compound isoelectronic of anthracene) in different solvents using the third harmonic of a neodyme laser (352.7 nm). The system to be studied is exposed to a pulse of the laser light and the transient absorption changes in the system (due to triplet polulation) are recorded. Knowing the extinction coefficient of the triplet (ϵ_{T-T}) and the total light absorbed, an absolute value of the triplet yield is obtained. The number of photons absorbed is determined by using a standard for comparison. In this work anthracene in ethanol has been used: the quantum yield Φ_T and the extinction coefficient of the triplet state have been very well established for this molecule: $\Phi_T = 0.7$ [1] and $\epsilon_{T-T} = 60.000$ in ethanol at 421 nm.

The method was used to determine triplet yields for acridine in polar and non-polar solvents: Benzene, tert-Butanol and water (pH = 12). Values of the quantum yields are given in the table. The corresponding ϵ_{T-T} were determined by a light saturation technique [2].

The different deactivation processes of the excited state S^* is expressed in the following scheme:

$S^* \rightarrow S_0 + h\nu$	Φ_F
$S^* \rightarrow$ photochemical reaction	Φ_R
$S^* \rightarrow T$	Φ_T
$S^* \rightarrow S_0$	Φ_{ic}