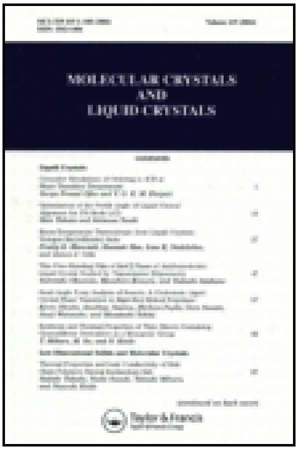

Molecular Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: I. B. Berlman (1968): Factors relevant to a short lifetime of an aromatic molecule: empirical data, Molecular Crystals, 4:1-4, 157-163

To link to this article: http://dx.doi.org/10.1080/15421406808082907

Molecular Crystals, 1968. Vol. 4, pp. 157–163

Printed in Germany

Factors relevant to a short lifetime of an aromatic molecule: empirical data*

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Certain of the presently known aromatic molecules, for example, p-terphenyl and PBD, have relatively fast fluorescence rise and decay times. However, to keep pace with recent developments in fast electronic circuitry and in photomultiplier tubes, scintillators are needed with even faster decay times. Some factors relevant to a short lifetime will be discussed—mainly from an empirical viewpoint.

Several years ago evidence[1] was presented indicating that in certain linear systems the fluorescence lifetime decreases as the molecular length increases. An obvious interpretation of this observation lies in the fact that the molar extinction coefficient ε increases with molecular size. One system considered at that time was the *p*-oligophenylenes, specifically, its first three members, diphenyl, p-terphenyl and p-quaterphenyl. These molecules and others in this series of homologs, which include some of the best scintillators produced to date, are called linear molecules and will be discussed further below. Other currently popular scintillators with fast fluorescence decay times, for example, POPOP and BPSB,† are also linear molecules with uninterrupted conjugation along the length of the molecule.

The natural fluorescence lifetime τ_0 of an aromatic molecule can be computed from its molar extinction coefficient ε and certain other parameters of its absorption spectrum. Several people have been involved in the development of this relationship, and a brief mention will be made of their contributions. In 1917 Einstein[2] derived a fundamental relationship between the transition probability for absorption and the transition probabilities for spontaneous, and induced emission. Ladenburg[3] and Tolman[4] proposed various relationships for atoms in gases and

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† Work performed under the auspizes of the U.S. Atomic Energy Commission.

‡ BPSP is Bis (Isopropylstyryl) benzene sold by the Pilot Chemical Company, 36 Pleasant Street, Watertown, Mass.

Perrin[5] for molecules in a liquid medium. The formula developed by Perrin has the form,

$$\tau_0^{-1} = Kn^2\nu_{\max}^2 \int \alpha \mathrm{d}\nu \tag{1}$$

where K is a constant, n is the index of refraction of the liquid, ν is a wave number in cm^{-1}, $\nu_{\max}$ is the mean wave number of the fluorescence band, and α is the absorption coefficient. Lewis and Kasha [6] used a similar equation to compute a phosphorescence lifetime in fluid media,

$$\tau_0^{-1} = K'n^2\nu_{\max}^2 (g_1/g_u) \int \varepsilon \mathrm{d}\nu \tag{2}$$

where K' is a constant, $\nu_{\max}$ is the wave number in cm^{-1} at the maximum value of the absorption band, g_1 and g_u are respectively the multiplicities of lower and upper states, and ε is the molar extinction coefficient in liters/mole-cm. These authors assume that the fluorescence quantum yield Q is unity, and that an adjustment is required when this is not the case.

Several authors have modified Eq. 2 in an attempt to correct for the experimental fact that for aromatic molecules the fluorescence spectrum is always displaced to wavelengths longer than those of the absorption spectrum. Förster[7] developed the equation

$$\tau_0^{-1} = K''n^2 \int \frac{(2\nu_0 - \nu)^3}{\nu} \varepsilon \mathrm{d}\nu \tag{3}$$

where K' is a constant, ν_0 is the wave number of a line of mirror symmetry between the fluorescence and absorption spectra, and ε is the decadic molar extinction coefficient. Strickler and Berg[8] proposed the following formula

$$\tau_0^{-1} = K'''n^2 \langle \nu_f^{-3} \rangle_{\mathrm{av}}^{-1} (g_1/g_u) \int \varepsilon \nu^{-1} \mathrm{d}\nu \tag{4}$$

where K''' is a constant, and

$$\nu_f^{-3} = \int \frac{f \mathrm{d}\nu}{f \nu^{-3} \mathrm{d}\nu} .$$

The other symbols have the same definitions as above.

Eqs. 3 and 4 can be written in a tractable form very similar to Eq. 2,

$$\tau_0^{-1} = K'n^2\nu_0^2 \int \varepsilon \mathrm{d}\nu$$

where the symbols have the same definitions as in the other equations. If the variation in n among the measurements is small it can be neglected as an important parameter in influencing the ultimate value of τ_0. In all of our measurements, the variation in n has been minimized by using a standard solvent, cyclohexane, If $\int \varepsilon d\nu$ is replaced by $\Delta\nu\, \varepsilon_{\max}$, where $\Delta\nu$ is the half-width of an absorption band and is assumed to have the same value for all molecules, and $\varepsilon_{\max}$ is the maximum value of the molar absorption coefficient, then it becomes apparent that for different molecules τ_0^{-1} is proportional to $\nu_0^2\varepsilon_{\max}$. This relationship is apparent from Figs. 1 and 2 which include data of τ_0, ν_0 and $\varepsilon_{\max}$ for more than 70 aromatic molecules made available from an independent study.[9] Values of τ_0 *vs* $\nu_0^2\varepsilon_{\max}$ and τ_0 *vs* $\varepsilon_{\max}$ have been plotted in log-log form

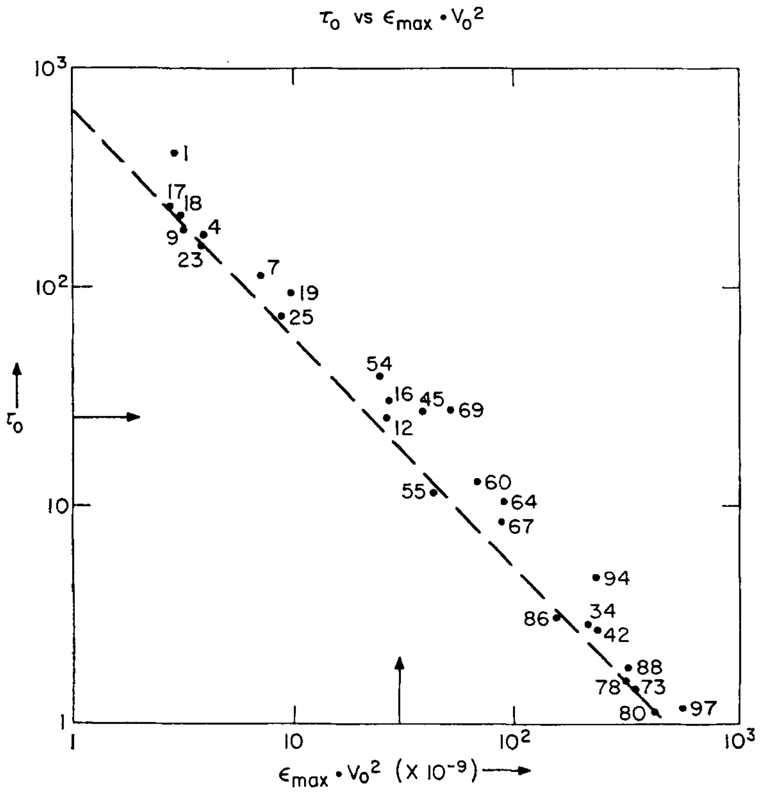

Figure 1. Plot of values of τ_0 in nsec as computed from Eq. 3 versus $\nu_0^2\ \varepsilon_{\max}$. Key to the numbers in the graph are found in the index of ref. 9.

and a straight line drawn so that essentially all of the points lie either on the line or above it. So that there is space for labelling, only a few of the 70 points are indicated, the remainder fall on the line or very near it. This process of elimination has unfortunately resulted in emphasizing those points lying away from the straight line, points which upon inspection are found to represent molecules with a common feature: their absorption spectra are structured. As might be expected, for such molecules, replacement of $\int \varepsilon d\nu$ with $\Delta\nu\varepsilon_{\mathrm{max}}$ gives undue weight to the value of the absorption peak maximum.

Figure 2 is useful in providing a simple means of estimating τ_0 when $\varepsilon_{\mathrm{max}}$ is known. Several precautions must be exercised and these will be discussed later. Another useful feature of this graph is indicated by the

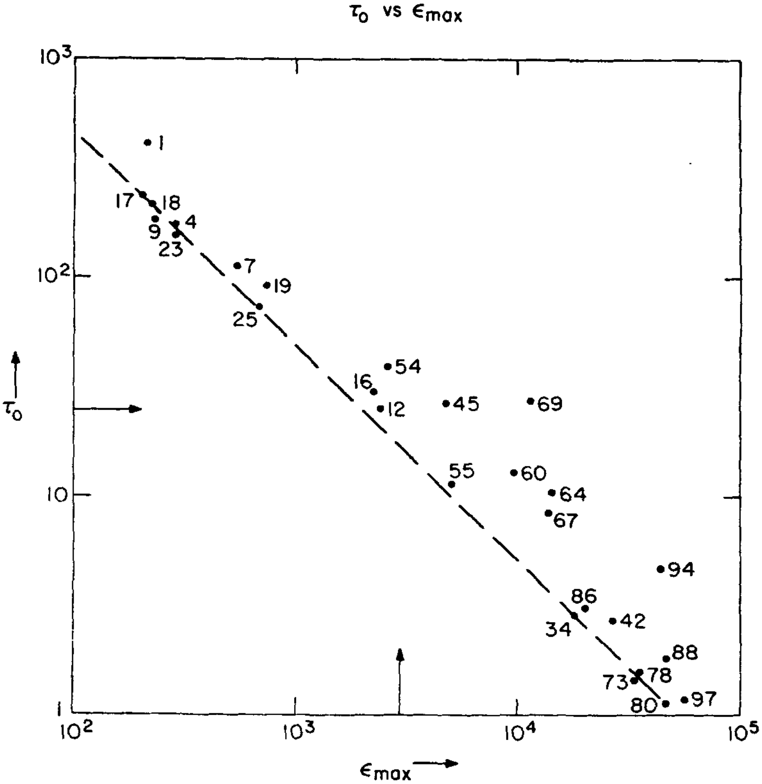

Figure 2. Plot of values of τ_0 versus $\varepsilon_{\mathrm{max}}$. Key to the numbers in the graph are found in the index of ref. 9.

arrows at the sides. Arrows have been placed to indicate qualitatively empirical limits of ${}^1L_b$, ${}^1L_a$, and ${}^1B$ transitions (Platt notation).[10] In ${}^1L_b$ transitions generally $\varepsilon_{\max} < 3000$ liter/mole-cm and $\tau_0 > 25$ nsec, in ${}^1L_a$ transitions $3000 < \varepsilon_{\max} < 50{,}000$ and $25 > \tau_0 > 2$ nsec, and in ${}^1B$ transitions apparently $\varepsilon_{\max} > 50{,}000$ and $\tau_0 < 2$ nsec.

Although ν_0^2 is one of the parameters affecting τ_0, a larger ν_0 tending to give a smaller τ_0, the variation in ν_0 from molecule to molecule is generally much less than the variation in $\varepsilon_{\max}$. It is apparent from Fig. 2 that $\varepsilon_{\max}$ can vary over many orders of magnitude; it is therefore the more important parameter in the determination of τ_0. For τ_0 to be small, $\varepsilon_{\max}$ must be large; however, though this is a necessary condition, it is not sufficient condition. Instances in which there is a large value of $\varepsilon_{\max}$ without a corresponding small value of τ_0 include 1) molecules having hidden transitions, 2) nonlinear molecules having partially hidden transitions, 3) molecules with isolated chromaphores and 4) molecules whose chromophores are essentially isolated from each other by steric hindrance. Biphenyl[11] is an example of a molecule which has a relatively large value of $\varepsilon_{\max}$, 17,000 liters/mole-cm; therefore, from Eqs. 3 or 4 or Fig. 2, it should have a short lifetime, approximately 3 nsec. Yet from the measured value of the fluorescence decay time τ and the quantum yield Q of biphenyl, about 16 nsec and 0.18, respectively, $\tau_0 = \tau/Q = 90$ nsec, and there exists a discrepancy of a factor of 30. To explain this anomaly a hidden level of much lower intensity and slighly lower energy than that of the intense masking-absorption band has been postulated. It is seen from Fig. 2 that a transition for which τ_0 is about 90 nsec corresponds to an $\varepsilon_{\max}$ of only about 600 liters/mole-cm.

Certain non-linear molecules, such as 1,3,5,-tri (biphenylyl-4)-benzene, o-biphenylyl benzene, and 1,3,5,-triphenylbenzene[12] have either hidden levels or partially hidden levels. These molecules have large values of $\varepsilon_{\max}$ and also large values of τ_0. 1,3,5-tri(biphenylyl-4)-benzene has an $\varepsilon_{\max}$ of about 100,000 liters/mole-cm, yet its τ_0 is about 20 nsec.

Certain molecules have their active chromophores separated by an inactive group. Thus diphenylmethane has its two phenyl groups separated by an insulating methylene group. Apparently resonance between the phenyl rings does not take place across the methylene group; instead, each phenyl group absorbs and emits radiation independently with the same characteristics as does toluene. Although the fluorescence quantum yield and decay time of diphenylmethane are approximately the same as those of toluene, τ_0 of diphenylmethane as computed from its $\varepsilon_{\max}$ is too small by a factor of about 1/2. Polystyrene is another example. For this molecule, to compute a meaningful τ_0 in agreement with τ and Q it is necessary to consider just the ε values of a chain segment corresponding to ethylbenzene.

When molecules have chromophores contiguous but essentially isolated from each other by steric hindrance, the π-electron system of one chromophore cannot interact effectively with the other chromophore, in other words, the conjugation between the chromophores is interrupted. Absorption and fluorescence characteristics of these molecules should be similar to the molecules mentioned above, in which the chromophores are isolated by an insulating group. Two examples of molecules in which the chromophores are nonplanar due to steric hindrance are bimesityl and biduryl. Measurements have not been made on these, but the author would be very surprised if the results were not as predicted.

These anomalies are at least theoretically avoidable if in the computation of τ_0 from Eqs. 2–4 the integration of ε is made over the correct absorption band, the one corresponding to the transition leading to fluorescence. Supplementary data are often needed to determine the transition of interest.

How large can $\varepsilon_{\max}$ become? Braude[13] calculated extinction coefficients for allowed transitions from considerations of effective "chromophore area". His theory is based solely on molecular geometry, the only assumptions being that light must fall within the space of the molecular dimensions to be absorbed and the transition has to be an allowed transition. For a molecule with a cross-sectional area of 10 A^2, $\varepsilon_{\max}$ is about 90,000 liter/mole-cm. Bowen[14] arrived at approximately the same value for $\varepsilon_{\max}$ using a classical argument that the maximum value of the oscillator strength is one.

From classical theory the one-dimensional oscillator strength f of a transition can be calculated from the equation

$$f = 4.32 \times 10^{-9}\, n \int \varepsilon d\nu. \tag{6}$$

It is of interest to compare the f value of one of our fastest scintillators, $1^2,2^3,5^2,6^3$-tetramethylsexiphenyl, with the classical limit of 1. This molecule has an $\varepsilon_{\max}$ of 64,000 liters/mole-cm and a τ^0 of 0.81 nsec (from Eq. 4). It turns out that f for the sexiphenyl molecule from Eq. 6 is 2.56. Thus we are close to a limiting value of f. It is not known whether a slightly longer p-oligophenylene such as p-octaphenyl, if solubility problems can be overcome, would have even larger values of $\varepsilon_{\max}$ and f and therefore a τ_0 less than 0.8 nsec.

As the p-oligophenylenes get longer they will eventually reach a size where they are no longer linear and a further increase in size should not result in an increase in $\varepsilon_{\max}$. Whether such a possibility is tied in with the absorption and fluorescence limits of long p-oligophenylenes mentioned by Dr. H. Wirth[15] and by the classical limitation of $f \simeq 1$, is not known.

The p-oligophenylenes appear to possess all of the characteristics favorable for short decay times. In particular, 1^2, 2^3, 5^2, 6^3-tetramethylsexiphenyl is probably the fastest scintillator in use today. The molecule is linear with uninterrupted conjugation throughout its length. Not only does it have a high $\varepsilon_{\max}$ but the center of gravity of the fluorescence-spectrum occurs at 3800 A, so that ν_0 is also large. In addition to other attributes this molecule has a high quantum yield.

Of course, if in a particular experiment fluorescence intensity can be sacrified, then through internal or external quenching one can reduce the quantum yield Q and thus, as seen by the equation $\tau = \tau_0 Q$, reduce the fluorescence decay time τ.

I should like to thank Dr. H. O. Wirth for stimulating discussions and for generous samples of o-biphenyl benzene, 1,3,5-tri(biphenylyl) benzene and 1^2,2^3,5^2,6^3-teramethylsexiphenyl. The author is also very grateful to Mr. W. R. Anderson for his many comments.

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