

FATE OF THE EXCITATION ENERGY IN THE QUENCHING OF FLUORESCENCE BY CONJUGATED DIENES†‡

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INTRODUCTION

Recently we have reported that the fluorescence of many aromatic hydrocarbons, and notably that of anthracene and naphthalene derivatives, is strongly quenched by conjugated dienes in solution¹⁻³. This phenomenon has been discussed in rather general terms and the particular interactions leading to singlet quenching are not as yet fully understood.

Our attention was first directed to this problem when measured quantum yields in certain photoreactions sensitized by aromatic hydrocarbons fell short of the values which we anticipated. Inspection of representative data,

Table 1. Quenching of fluorescence of aromatic hydrocarbons by dienes

<i>Aromatic</i>	<i>Diene</i>	$[\text{Diene}]_{\frac{1}{2}}^{\dagger}$ M $\times 10^3$	k_q^{\ddagger} M ⁻¹ sec ⁻¹ $\times 10^{-9}$
Naphthalene	2,5-Dimethyl-2,4-hexadiene	2.63	3.96
Naphthalene	1,3-Cyclohexadiene	3.95	2.50
Naphthalene	4-Methyl-1,3-pentadiene	8.76	1.20
Naphthalene	<i>trans</i> -2- <i>trans</i> -4-Hexadiene	16.8	0.62
Naphthalene	<i>trans</i> -2- <i>cis</i> -4-Hexadiene	20.5	0.51
Naphthalene	<i>cis</i> -2- <i>cis</i> -4-Hexadiene	45.3	0.23
Naphthalene	3-Methylene cyclohexene	61.2	0.17
Naphthalene	<i>trans</i> -2-Methyl-1,3-pentadiene	94.2	0.11
Naphthalene	<i>trans</i> -Piperylene	95.0	0.11
Naphthalene	<i>cis</i> -Piperylene	113	0.092
Naphthalene	2,3-Dimethyl-1,3-butadiene	680	0.015
1-Methylnaphthalene	1,3-Cyclohexadiene	12	1.1
Anthracene	1,3-Cyclohexadiene	67	2.96

† Concentration required to quench half the fluorescence.

‡ Calculated assuming τ_f for naphthalene = 77 nanoseconds as estimated by oxygen quenching.

illustrated by those shown in *Table 1*, shows that in many cases the quenching is quite strong and in some cases approaches the diffusion controlled rate. Additional data are presented in ref. 3.

In this report we will discuss quantitative balance studies that have been carried out in several cases, designed to learn what happens to the quencher. Although the cases reported show that quenching does not involve significant

† This paper may be considered Part L of the series "Mechanisms of photochemical reactions in solution".

‡ Contribution No. 3542 from the Gates and Crellin Laboratories.

chemical change in the quencher, we do not wish to imply that this result is entirely general.

RESULTS

Figure 1 shows a plot of data obtained in the study of the quenching of the fluorescence of anthracene by *trans*-piperylene. The relative intensity

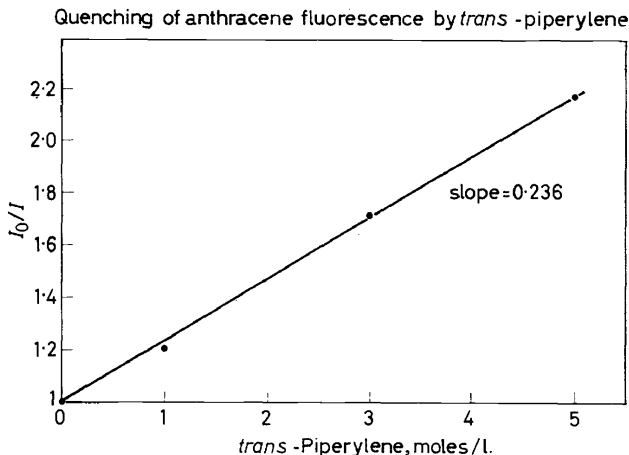
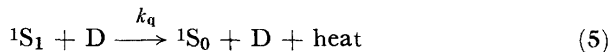


Figure 1. Stern-Volmer treatment of data for quenching of fluorescence of anthracene by *trans*-piperylene

of fluorescence is easily measured by comparison of the emission intensities at any wavelength, since reduction in fluorescence occurs with no detectable change in the shape of the spectrum. The fit to a Stern-Volmer relationship indicates that the following mechanism is adequate to describe the decay of the lowest excited singlet state of anthracene:



S = sensitizer

D = diene

k_u = sum of rate constants for all other first-order decay processes, including chemical reaction and internal conversion.

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We were indeed fortunate that quenching of fluorescence of almost any material by oxygen appears to be diffusion-controlled⁴. As a consequence, a reasonable estimate of the lifetime of excited singlets in solution can be made by merely measuring the relative intensity of fluorescence in the presence and in the absence of oxygen.

$$\frac{\phi_{fo}}{\phi_f'} = 1 + k_q' \tau_s [\text{O}_2] \quad (7)$$

ϕ_{fo} = quantum yield of fluorescence in the absence of known quenchers

ϕ_f' = quantum yield of fluorescence in the presence of oxygen

$$\tau_s = \text{lifetime of the excited singlet} = \frac{1}{k_f + k_{is} + k_u}$$

Berlman has confirmed the validity of the assumption that k_q' is virtually independent of the nature of the quencher for a large number of compounds⁵. The value of 3.4×10^{10} for k_q' has been suggested by Berlman and we have used this in the calculation of values of k_q for quenching by dienes. The number seems a little higher than might be expected, but a small change in the rate constant assigned for oxygen quenching would only change all of our calculated rate constants by the same small factor.

Sensitized isomerization of piperylene has been used to count triplets formed by intersystem crossing by excited molecules⁶. Since concentrations of the diene used in some quenching experiments are large enough to quench fluorescence of some of the compounds studied, there was obvious need to study the relationship between sensitized isomerization and fluorescence quenching. Naphthalene is a case in point. The compound is quenched to a significant extent by even a quencher as impotent as piperylene, largely because τ_s for naphthalene is fairly long (9.6×10^{-8} sec)⁵. The matter is especially important since the earlier work indicated that the sum of the quantum yields for fluorescence and intersystem crossing is less than unity⁶. If we assume that fluorescence quenching does not lead to the characteristic triplet reactions of the quencher, we can formulate the following relationship:

$$\phi_x = \phi_{ico} \frac{\phi_f'}{\phi_{fo}} \alpha \beta \quad (8)$$

ϕ_x = quantum yield for the sensitized reaction

ϕ_{ico} = quantum yield of triplets in the absence of quencher

α = the fraction of the sensitizer triplets that transfer energy to the diene

$$= \frac{k_{tr}[\text{D}]}{k_{dt} + k_{tr}[\text{D}]}$$

k_{dt} = rate constant for decay of sensitizer triplets

$$\beta = \text{the fraction of the diene triplets that undergo the chemical change}$$

$$= \frac{R_r}{k_{dt} + R_r}$$

R_r = rate of the reaction, which is a function of the concentration of some reactant.

Equation (8) is written in a generalized form suitable for use in the study of any photosensitized reaction. The factor α can ordinarily be made close to unity with sensitizers having triplet excitation energies above 55 kcal/mole. Rate constants for quenching such triplets by conjugated dienes are $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ or higher^{7, 8}. Consequently, if the sensitizer triplet has a lifetime of 10^{-3} sec or higher, the efficiency of triplet energy transfer is greater than 99 per cent with diene concentrations about 10^{-4} M . The factor β must be determined by study of the particular photoreaction, usually using data obtained with sensitizers such as benzophenone which have high triplet energies and undergo intersystem crossing with 100 per cent efficiency under all known conditions⁶. If the reaction of the chemically reactive triplet is bimolecular, as in the case of sensitized dimerization⁹, β will be a function of diene concentration. In the case of *cis* \rightleftharpoons *trans* isomerization, β is the triplet decay ratio^{6, 10}. If the assumption that quenching of excited singlet states of the quencher is exclusively an energy-wasting step is correct, the value of $(\phi_x/\phi_{t0} \alpha\beta)$ should be equal to ϕ_t/ϕ_{t0} . On the other hand, if quenching of singlets produces states of the diene that can undergo isomerization, one or more additional terms will appear in Eq. (8) and the extent of quenching of the chemical reaction will not be equal to fluorescence quenching. In the cases reported in this paper, Eq. (8) correlates the data so, for the sake of simplicity, we will present our results as tests of the equation. We do not necessarily expect this to be generally true.

cis-trans Isomerization

Table 2 shows quantum yields for isomerization of *cis*- and *trans*-piperylene by naphthalene. Figure 2 shows a plot of the data obtained with *cis*-piperylene and naphthalene. Extrapolation to zero concentration of piperylene indicates that the limiting value of $\phi_{c \rightarrow t}$ is 0.37. Of course, real data obtained in the low concentration region would not approach the intercept, because the value of α would begin to decrease in a region much beyond that covered by the present measurements. A test of Eq. (8) is provided by Figure 3. The solid line is the locus of the calculated values using the limiting value of $\phi_{c \rightarrow t}$ and kinetic parameters for quenching of naphthalene by *cis*-piperylene as entered in Table 1. The experimental points lie along the curve well within the limits of experimental error. The result implies that within our experimental accuracy there is no evidence for isomerization of piperylene concomitant with quenching of fluorescence.

The ratio of $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$ measured with high energy sensitizers is 1.25^{10} . Consequently, the apparent limiting value of $\phi_{t \rightarrow c}$ calculated by reference to the data for *cis*-piperylene is 0.30. However, examination of the three data in Table 2 for the sensitized *trans* \rightarrow *cis* reaction indicates that the

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quantum yields are a little lower than would be expected. A triplet decay ratio of 1.50 would fit the data better than 1.25. The reason for this apparent discrepancy cannot be unequivocally assigned with the limited data at hand. There may be some small amount of isomerization accompanying

Table 2. Quantum yields of *cis-trans* isomerization of piperlyene sensitized by naphthalene

Diene	ϕ_t/ϕ_o	ϕ
<i>cis</i> -1,3-PENTADIENE		
0.01 M	0.92	0.34
0.02	0.85	0.31
0.05	0.69	0.23
0.08	0.59	0.20
0.12	0.48	0.17
0.20	0.36	0.11
1.00	0.10	0.06
<i>trans</i> -1,3-PENTADIENE		
0.08	0.54	0.13
0.12	0.46	0.11
0.20	0.32	0.07

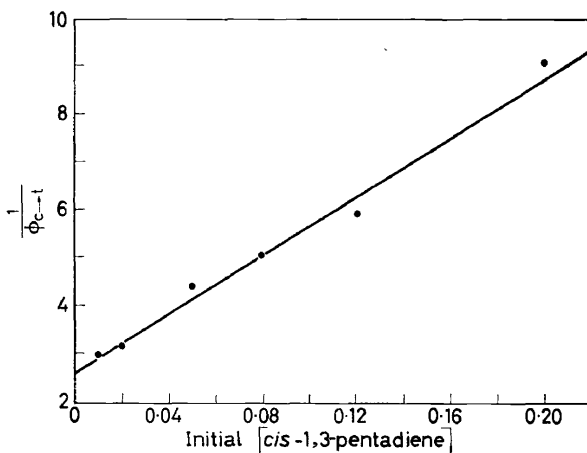


Figure 2. Reciprocal of the *cis* \rightarrow *trans* quantum yield as a function of initial 1,3-pentadiene concentration

quenching[†] or the decay ratio may actually be slightly different for triplets produced by high energy sensitizers, such as benzophenone, and those having intermediate excitation energies, such as naphthalene.[‡] Use of the

[†] If a small amount of *cis* \rightarrow *trans* reaction occurs during quenching by *cis*-piperlyene, the extrapolation of Figure 2 would be in error; reduction of the limiting value of $\phi_{c \rightarrow t}$, from 0.37 to 0.34 would bring the results into closer agreement.

[‡] We have anticipated this phenomenon. Study of the sensitized dimerization of isoprene and butadiene⁹ shows that two kinds of triplets, *s-cis* and *s-trans* can be produced. Sensitizers having less than 60 kcal/mole of excitation energy become selective in their action and seek out *s-cis* molecules. The piperlyenes should show similar behaviour, so we expect naphthalene ($E_T = 61$) to produce relatively large amounts of *cis* triplets in comparison with high energy sensitizers. That the decay ratios for *cis* and *trans* triplets should be different is not surprising.

decay ratio of 1.50 gives $\phi_{t \rightarrow c} = 0.25$ and the sum of the two quantum yields is 0.61. The latter figure should be a measure of the efficiency of intersystem crossing by naphthalene in the absence of singlet quenchers. The value is considerably higher than that previously estimated⁶ and is in reasonably good agreement with the value of 0.8 reported by Medinger and Wilkinson¹¹ who have developed an elegant method based upon correlation of measurement of enhancement of triplet concentrations seen by flash spectroscopy with attenuation of fluorescence yields in heavy atom solvents.

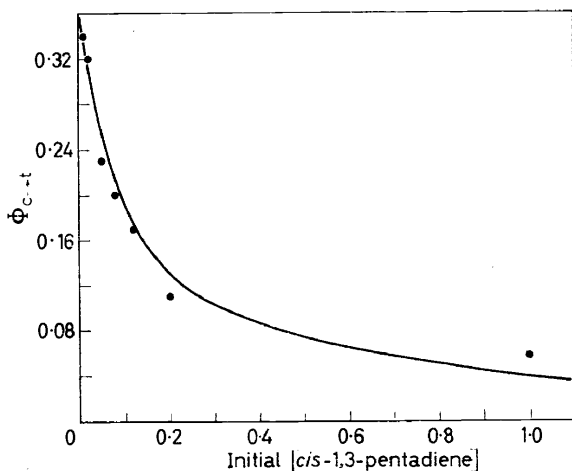


Figure 3. *cis* \rightarrow *trans* Quantum yield as a function of initial 1,3-pentadiene concentration

Quenching of dimerization of cyclohexadiene

Sensitized dimerization of 1,3-cyclohexadiene follows a pattern that has become familiar in sensitized photocycloaddition reactions¹². Triplet energy transfer is clearly implicated and quantum yields approaching unity are obtained using benzophenone as a sensitizer at moderate levels of the diene concentration[†]. Because naphthalene interferes with the vapour chromatographic determination of the yields of dimeric products, the reaction was studied using 1-methylnaphthalene as the sensitizer. The following is a summary of results:

Diene concentration	0.21
$\beta([D] = 0.21)$	0.88
ϕ_{ic}	0.60 [‡]
ϕ_t/ϕ_{to}	0.054
ϕ_{Dimer} (obs.)	0.028
ϕ_{Dimer} (calc.)	0.029

[‡] The value of 0.48 reported earlier⁶ has been corrected using measurements of the quenching of fluorescence of 1-methylnaphthalene by *cis*-piperylene.

The result demonstrates that chemically active states of cyclohexadiene are not produced in the quenching action. Although naphthalene was

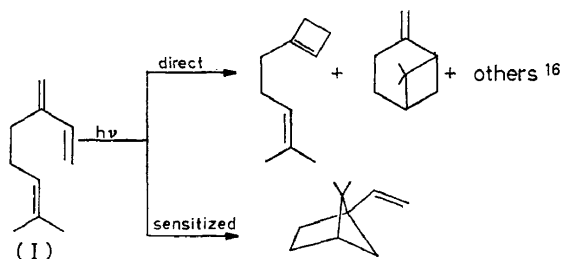
[†] $\phi = 0.88$ with 0.2 M diene.

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not studied in detail because of the analytical problem, the behaviour of the compound is very similar to that of the α -methyl derivative. In the original investigation of diene dimerization¹³ naphthalene was found to be a very inefficient sensitizer for reasons that were then unaccountable. In the study of the piperlyenes described above, we observed that no more than traces of dimeric products were obtained in experiments with sufficiently high concentrations of dienes to give substantial yields of dimers with most high energy sensitizers¹⁴.

Cyclization of myrcene

Myrcene (I) undergoes photocyclization as a consequence of both sensitized¹⁵ and direct excitation^{16, 17}. The compound is an especially interesting probe for electronic excitation transfer reactions since direct and sensitized excitation give rise to different products, implying that excited singlets and triplets have different chemical properties.



Myrcene is not a very reactive quencher toward naphthalene; half quenching occurs at 0.29 M diene. At high concentrations some higher order reaction must occur to at least a limited extent since an intractable gum is deposited on the walls of the vessel. However, trends in the quantum yields of cyclization products probably remain significant. Solutions containing the triene (0.5 M, 1.0 M, and 5.0 M) and naphthalene were degassed and irradiated for long periods of time with 3130 Å light; at 0.5 M the normal product of sensitized reaction was easily detected by vapour chromatography; a reduced yield was observed at 1.0 M; none could be detected at 5.0 M. Other cyclization products were not detectable in any of the experiments.

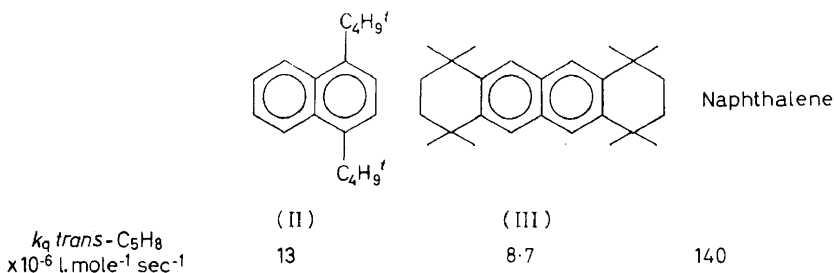
Photochemistry of the excited singlet states of the dienes

Conjugated dienes apparently undergo intersystem crossing from excited singlets to triplets with very low efficiency¹⁸. This is evident from the products of direct irradiation of the piperlyenes, myrcene, and 1,3-cyclohexadiene formed under direct irradiation. As has been described by Dauben and Wipke¹⁷, numerous products, having only limited overlap with the products of sensitized reactions, are formed. Although we were easily able to measure quantum yields of characteristic triplet products down to 0.02, we could not even detect the singlet products in any experiments using aromatic hydrocarbons as sensitizers.

DISCUSSION

The data presented above indicate fairly clearly that quenching of the excited singlet states of aromatic hydrocarbons by conjugated dienes does not lead to production of major amounts of electronically excited states of the quenchers. In fact, the data are compatible with the conclusion that no electronic excitation is transferred, but are not sufficiently precise to exclude the formation of small amounts of diene triplets. In some cases we have observed formation of new products having the composition of adducts from the quenchee and the quencher. Structural study of the photoadducts is incomplete at present and will be presented elsewhere. However, the photoadducts appear to be of the same general type as those reported by Koltzenburg and Kraft¹⁹. The quantum yields for new products are low in all cases and are entirely negligible with many of the pairs included in this work. When new products are formed, their appearance parallels fluorescence quenching closely, so we presume that chemical combination is an occasional consequence of the destruction of singlet states of aromatic compounds by dienes.

For the most part, *quenching must be described as catalysis by the dienes of the non-radiative decay of the quenchees*. The rates observed do not exceed those expected in diffusion-controlled reactions, although the highest values approach that limit fairly closely. Results reported earlier³ show that addition of alkyl substituents to naphthalene reduces sensitivity to quenching. The effect was especially pronounced with compounds (II) and (III).

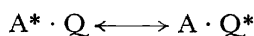


We tentatively conclude that quenching not only requires that the two molecules be in contact but that the contact be sufficiently intimate to be subject to steric hindrance. The pattern of response to addition of methyl groups as substituents on the diene is clearly a combination of many factors. In general, addition of methyl groups increases reactivity but there are interesting irregularities. Addition of a terminal methyl in the *trans* orientation produces a greater increase in quenching reactivity than does introduction of a methyl in the 2- or 3- positions or in the terminal *cis* configuration. Furthermore, as was previously noted, naphthalene and anthracene show very similar sensitivities to variation in the structure of the quenchers³.

Weil-Malherbe and Weiss suggested in 1944 that fluorescence quenching involves formation of a charge transfer complex between quencher and quenchee²⁰. This notion has been developed further by Ferguson²¹ and by Hochstrasser²². These discussions are somewhat unsatisfying on two grounds. First, the emphasis is put on consideration of the binding energy

of the complex. Although some binding is obviously desirable to give the complex a lifetime within which to decay, the mere invocation of binding does not *per se* explain their very rapid decay rates. Since we have been unable to detect any sign of new emission due to complexes, we infer that they must have very fast non-radiative decay rates, very likely 10^{10} sec^{-1} or faster in some cases[†]. Murrel and Tanaka have pointed out the probable importance of other configurations in delocalizing excitation between partners in excited complexes²³.

We have developed a model which is really the same as that of Murrel except for the introduction of considerable structural detail designed to account for some of the reactivity relationships observed. The result turns out to be closely related to a model used very recently by Salem²⁴ to calculate interaction energies in excited complexes. As a basis we will assume that within the complex at least a small amount of the electronic excitation is transferred to the quencher.



Since the $S_0 \rightarrow S_1$ excitation energies of conjugated dienes are considerably greater than those of the quenchers²⁵ we expect that the contribution from the second configuration will be rather small. However, *we visualize the importance of the $A \cdot Q^*$ structure as arising primarily from its effect on the rate of internal conversion*, rather than from a major contribution to the binding energy. Weak coupling may allow the excited complexes to borrow some of the very rapid, non-radiative decay characteristics of the dienes. Even though we cannot give a definitive description of the source of that property of excited diene molecules[‡], we at least know that the characteristic is there to be borrowed. This suggestion implies that coupling to vibrational modes of the quencher assists internal conversion.

We furthermore suggest that the specific relative orientation of an acyclic diene and naphthalene shown in *Figure 4* is optimum for quenching. Although the model has interesting possibilities for establishing electronic

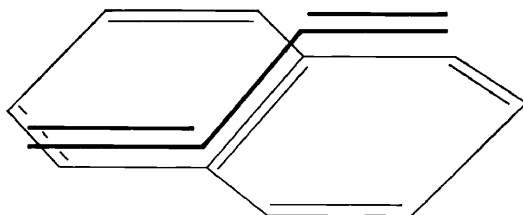


Figure 4. Optimum geometry for interaction

communication between the partners, it is really chosen to account for steric effects. The generalized model predicts that there should be a correlation between quenching reactivity and the $S_0 \rightarrow S_1$ excitation energies

[†] This rather sloppy figure is arrived at by estimating that fluorescence with intensity as high as a few per cent of the emission from the parent hydrocarbons could be detected.

[‡] For formulation of a theory of non-radiative transitions see G. W. Robinson and R. P. Frosch. *J. Chem. Phys.* **37**, 1962 (1962); G. W. Robinson and R. P. Frosch. *J. Chem. Phys.* **38**, 1187 (1963); and G. W. Robinson. *J. Chem. Phys.*, in press.

of the dienes. In looking for such a correlation we have been forced to use positions of the maxima in the first absorption bands of the dienes, although O—O bands might be better. The latter are never resolved and, as Srinivasan has pointed out²⁶, the long wavelength tails in the spectra of dienes make the location of the onset of absorption uncertain. Furthermore, we believe that the absorption at longest wavelength may be contributed largely by *s-cis* forms and is irrelevant to the properties of the more abundant *s-trans* forms which are probably responsible for most of the quenching. In any event, the existence of Woodward's Rules²⁷ implies that the Franck-Condon maxima provide some measure of the variation in transition energies as alkyl groups are added to the diene structure. *Figure 5* shows

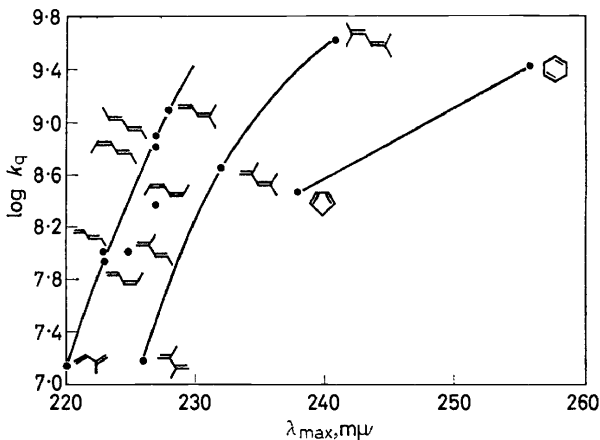


Figure 5. The correlation of quenching constants with diene singlet absorption maxima

$\log k_q$ for quenching of naphthalene fluorescence as a function of λ_{\max} for the dienes. Taken as a whole the data show no systematic relationship. However, the model in *Figure 4* suggests that groups attached to the diene system in terminal *trans* positions should offer less steric hindrance than groups in the terminal *cis* or central positions. If we introduce this prejudice a suggestion of a systematic relationship can be seen. A smooth correlation line can be drawn close to the points for compounds in which there are either none or only one of the unfavourable orientations of methyl groups. Within this group there is a fairly regular increase in quenching reactivity as the excitation energy of the diene is lowered. Furthermore, the three compounds in which there are two unfavourable interactions show about the same trend, except that the reactivity of the group as a whole is lower than that of the first group[†]. Finally, the two cyclic dienes do not correlate with the acyclic compounds. Based on their excitation energies alone, we might expect them to be more reactive than is observed[‡]. We

[†] We would, of course, be pleased if the first group could be divided in two, those having one unfavourable orientation and those having none. However, there is no justification in the data now available for attempting such a separation.

[‡] This observation is especially significant in the case of cyclopentadiene. The reactivity of cyclohexadiene is close to the diffusion-controlled limit where reactivity should cease to be a function of diene structure.

would expect this behaviour on the basis of our model, since the cyclic dienes cannot lie over the face of the naphthalene nucleus in the manner shown in *Figure 4*.

There are probably some symmetry requirements for mixing the states $A^* \cdot Q$ and $A \cdot Q^*$. At the present time we have insufficient data on quenching reactivity to warrant an attempt to develop a comprehensive theory. However, examination of the model shown in *Figure 4* prompts some preliminary observations. The lowest excited singlet state of naphthalene is ${}^1B_{3u}$ (ref. 28) and the lowest excited state of *trans*-butadiene is 1B_2 . Since the molecules belong to different symmetry classes one cannot combine them directly. However, it is interesting to note that the four centres in naphthalene (carbon atoms 1, 5, 9, and 10) that lie close to the four atoms of the diene in our model transform according to the B_2 operations of the symmetry class C_{2v} †. Unfortunately there is no set of four centres in anthracene arrayed in the *trans*-diene order which show exactly analogous transformation properties in the low lying ${}^1B_{2u}$ state. We hope to gather sufficient additional data to sustain definitive analysis at some future time.

SUMMARY

The fluorescence of aromatic hydrocarbons is quenched by conjugated dienes. Quantum balances have been carried out in several cases and indicate that quenching does not lead to significant amounts of chemical change, although adducts between the aromatic compound and the diene are produced in low quantum yield in some cases. A possible mechanism for catalysis of nonradiative decay of excited states is discussed.

ACKNOWLEDGEMENTS

This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479. We are indebted to Dr David G. Whitten and Mr George F. Vesley for both stimulating discussion and communication of the results of related experiments.

† This conclusion is reached by looking at the coefficients of the indicated centres in the naphthalene molecular orbitals usually labelled ψ_6 and ψ_7 . The latter must be chosen in preference to ψ_6 in order to make the excited state of naphthalene B_{3u} rather than B_{2u} . However, the same B_2 -like behaviour of the four centres is observed in the B_{2u} configuration since both ψ_6 and ψ_7 have nodes in the xz plane.

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