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(21) 1,2-Diphenyl-3,4-bis(acetoxymethyl)cyclobutene: λ_{sh} 228 nm (log ϵ 4.28), λ_{max} 290 (4.12); λ_{max} (fluorescence) 382 nm, $\lambda_{(excit)}$ 309 nm. 1,2-Diphenylcyclobutene:[22] λ_{max} 227 nm (log ϵ 4.38), 297 (4.26); λ_{max} (fluorescence) 380 nm, $\lambda_{(excit)}$ 317 nm. See also: G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **10**, 340 (1971).

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(31) In comparison, the ^{13}C–H coupling constant for C-1 of norbornane is 142 Hz and that for C-1 of norbornadiene is 146 Hz (L. M. Jackman and S. Sternhill, "Applications of NMR Spectra in Organic Chemistry", Pergamon Press, Elmsford, New York, 1969, p 346).

(32) The last set of spectra were run on a Jeol-100 instrument and the bands are sharper than those of Figure 1. The new spectra show a slight enhancement of the bands of form VIII at the expense of those of XV at −40 °C.

(33) In contrast, no reaction was observed between photoisomer A and dimethyl acetylenedicarboxylate at −40 °C during 48 h.

(34) A similar effect is noticed in *o*-terphenyl.

(35) (a) W. McCay and R. N. Warrener, *Tetrahedron Lett.*, 4779–4782 (1970); (b) *ibid.*, 4783–4786 (1970).

(36) Surprisingly, McCay and Warrener[35] report a singlet for the hydrogens on the cyclohexadiene ring of XVIIIb.

(37) (a) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964, pp 108–110. (b) Coupling among related hydrogens is also undetectable in cyclooctatetraene I.[12]

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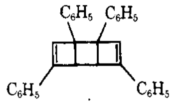
(40) In this context, it would be of interest to determine whether the thermal conversion of compound i to I[12] proceeds directly or via XV $\rightleftarrows$ VIII.



i

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Steric and Spin-Orbital Effects on the Photodimerization of Thianaphthene 1,1-Dioxide[1,2]

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Abstract: The quantum yields of dimerization of thianaphthene 1,1-dioxide and 2-bromothianaphthene 1,1-dioxide were measured at 313 nm as a function of substrate concentration in selected solvents. The dimerization of 2-bromothianaphthene 1,1-dioxide was sensitized by the crown ether complex of Rose Bengal and by Michler's ketone, but not by crystal violet. The dimerization of thianaphthene 1,1-dioxide shows reasonable linear Stern–Volmer quenching by cyclooctatetraene. The 2-bromothianaphthene 1,1-dioxide under similar quenching conditions with cyclooctatetraene yields data that produce a curved Stern–Volmer relation. The results of this study indicate that internal heavy atoms show a modest effect on both $T_1 \leftrightarrow S_1$ and $S_0 \leftrightarrow T_1$, but that the former process shows a greater sensitivity to external heavy-atom perturbation. An exciplex mechanism that competes with excited triplet state dimerization of 2-bromothianaphthene 1,1-dioxide is proposed to be consistent with all the available data. Rate constants for the multipathway scheme are derived and steric hindrance to ring closure is suggested as being a contributing factor to the inefficiency of the reaction.

External and internal heavy-atom effects on the photochemical processes of acenaphthylene and its derivatives have been the subject of several recent studies.[4] Because the effects upon acenaphthylene photochemistry have been dramatic, we have initiated studies to seek out and explore other molecules in which the heavy-atom effect might prove to be a viable experimentally detectable phenomenon.

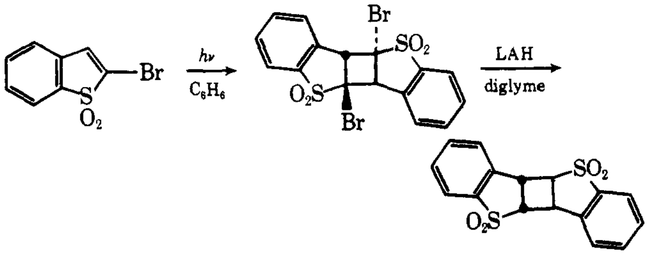
The mechanistic study of the photodimerization of thianaphthene 1,1-dioxide (TND) published by Harpp and Heitner[5] reported data that suggested to us that TND fit the criteria[4e] for a molecule that should manifest a photochemical heavy-atom effect. Indeed, the photodimerization of TND was found to show an external heavy-atom effect,[1b] and this encouraged us to broaden the study to include 2-bromothianaphthene 1,1-dioxide (BrTND).

The fact that the general phenomena of the heavy-atom effect may be more widespread in photochemistry than is generally recognized is illustrated by this study and by recent data reported for quite different structural systems.[6]

Results

A. Photoproducts. The only detectable photoproduct that results from irradiating 2-bromothianaphthene 1,1-dioxide (BrTND) in benzene has been identified as the trans-cyclobutane dimer derived from head-to-tail combination of BrTND (Scheme I). The high melting point of this dimer in conjunction with its extreme insolubility in all organic solvents precluded the use of the common analytical techniques of NMR, GLC, and high-pressure liquid chromatography in its structure proof. By pursuing the chemical approach used by

Scheme I



Heitner and Harpp[5] in the structure proof of TND dimers, we achieved a satisfactory structural analysis.

The dimer of BrTND was prepared in a 93% crude yield by irradiating a 0.045 M solution in benzene with 350-nm light. Infrared spectra of this crude dimer and the dimer that had been continuously extracted with hot benzene showed identical absorbances, suggesting that only one species was present. Besides the typical aromatic bands at about 1600 cm^{-1}, bands at 1311 and 1151 cm^{-1} characteristic of sulfones[7] were also observed. A satisfactory elemental analysis confirmed the presence of bromine in the dimer so that carbon–bromine photolytic cleavage is a reaction of minor concern in this study.

A mass spectrum of the solid photodimer shows a weak molecular ion grouping at *m/e* 488 with satellite peaks at M + 1, M + 2, M + 3, and M + 4, characteristic of a molecule containing two bound bromine atoms.[8] Two peaks grouped around M − 79 were 5% of the base peak *m/e* 137 and suggested the loss of a single bromine atom. These peaks of *m/e* 409 and 411 were of nearly equal intensity, reflecting the fact that a bromine atom was still contained in the new fragment.[8] A very weak set of lines at M − 64 suggested that a minor fragmentation pathway involved extrusion of SO_2. Peaks of 10% intensity of the base peak occurred at *m/e* 301, 302, 303, and 304. The identity of these fragments is not clear. The more intense lower molecular weight fragments in the photodimer spectrum correspond to the peaks found for the mass spectrum of monomeric BrTND.

The BrTND photodimer was treated with an excess of lithium aluminum hydride in refluxing diglyme while protected by a nitrogen atmosphere. An unanticipated selective reduction occurred in which only hydrogenolysis of the carbon–bromine bonds took place. The sulfone functions remained unaffected under these conditions. This reduced dimer was compared to an authentic sample of trans head-to-tail dimer of TND[5] and found to be identical in all respects, thus establishing the stereochemistry of the brominated precursor. This selective reduction in our hands by $LiAlH_4$ was verified by subjecting the trans head-to-tail dimer of TND to the same reaction conditions. In refluxing diglyme it remained inert.

It has been shown that $LiAlH_4$ in refluxing *n*-butyl ether does reduce the TND dimers to sulfides.[5] In a related study Numanov and co-workers[9] found that sulfone reduction occurred without hydrogenolysis of C–Br bonds when $LiAlH_4$ in tetrahydrofuran was used on *trans*-2,3-dibromo-2,3-dimethylthianaphthene 1,1-dioxide, a sterically hindered derivative of TND.

The possibility exists that in our system diglyme might behave like a partial crown ether and through specific solvation effects cause the result we have obtained. The granular size and activity of $LiAlH_4$ could also be a variable, influencing the unusual selective reduction of the dimer of 2-bromothianaphthene 1,1-dioxide.

We ultimately detected a second photodimer by irradiating a 0.05 M solution of BrTND in nitromethane at 350 nm. The dimerization proved inefficient in nitromethane. A period of 42 h of irradiation produced only 30% crude yield of photodimers whereas a 14-h irradiation in benzene under similar conditions produced a 93% crude yield.

A high-melting isomer crystallized on the surface of the tube during the irradiation of the nitromethane solution. This dimer proved to be identical in all respects with that isolated from the benzene irradiation. Upon evaporating the nitromethane solution to dryness and recrystallizing the residue from hot methanol, a second dimer was obtained. Its lower melting point of 272–276 °C and higher solubility in common solvents served to distinguish it from the high-melting anti head-to-tail photodimer. The low-melting dimer showed sufficient solubility in deuteriochloroform to allow a determination of its NMR spectrum. A singlet at δ 5.05 as well as a multiplet in the 7.2–7.8 region compares quite favorably with the reported NMR data for the anti head-to-head dimer of TND itself (δ 7.85–8.15 and 4.20–5.10).[5b]

A comparison of the infrared spectrum of the low-melting BrTND photodimer to the infrared spectrum of the anti head-to-head dimer of TND[5b] shows a similarity in pattern in the 900–450-cm^{-1} region and a dissimilarity to the TND head-to-tail dimer. We thus conclude that the second more soluble isomer isolated from nitromethane is the anti head-to-head photodimer of BrTND.

An attempted mass spectrum of this dimer in the solid probe of the spectrometer produced no M^+ peak. We anticipated that the mass spectrum would not produce the molecular ion because of the steric interactions that are probably extant in the anti head-to-head dimer. Thus, the dimer tends to cleave and fragment without forming a stable M^+ peak.

The great difficulty in unequivocally characterizing this head-to-head dimer means that its stereochemical identification must remain tentative until x-ray crystallographic data can be obtained.

A fortunate observation does allow us to state with confidence that the crude dimer isolated from the benzene solution is nearly 100% anti head-to-tail. We subjected this crude dimer to a refluxing deuteriochloroform treatment and ran a NMR spectrum of the slurry. Within the limits of the NMR measurement the more soluble isomer could not be detected in the slurry.

The nitromethane experiment was initiated by us to counter the objections of a referee who is concerned about the appearance of only one isomer in benzene. We have shown that a second isomer is absent and that it is not photolabile under conditions identical with those of the benzene irradiations.

We offer the following explanation. The previous investigators[5a] reported a large solvent polarity effect on the product distribution of head-to-head (H-H) and head-to-tail (H-T) dimers from TND. The charge–dipole in the excited state is maximized for head-to-head combinations and minimized for head-to-tail combinations.[5a] The addition of a bromine substituent at the 2 position of TND further enhances this dipolar charge distribution. Thus, in the nonpolar solvent benzene only a few charge–dipolar complexes of the head-to-head type are favored, and the transition-state free energy of head-to-head types is too high to lead to formation of head-to-head dimers. It is only when we turn to nitromethane, a very polar solvent, that any of the maximum dipolar head-to-head complex leads to product formation. Obviously. the steric bulk of the bromine atom also contributes greatly to the increased free energy of the transition state leading to the H-H dimer.

B. Concentration Studies. The quantum yield of dimerization of TND in bromoethane is enhanced compared to the solvent benzene.[5] In Figure 1 the inverse of the quantum yield of dimerization of TND (Table I) is plotted as a function of the reciprocal of the concentration of TND in bromoethane.

A similar treatment of the data for the dimerization of BrTND at 313 nm in benzene shows an apparent linear correlation (vide infra) (Figure 2, Table II). A wide range of concentrations of substrate could not be explored because both TND and BrTND monomers have limited solubility in the

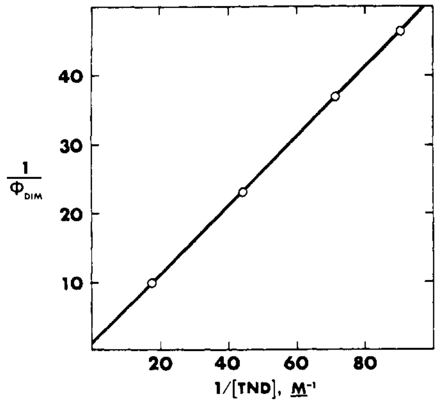


Figure 1. The dependence of ϕ_{DIM} upon different concentrations of TND undergoing dimerization at 313 nm in bromoethane.

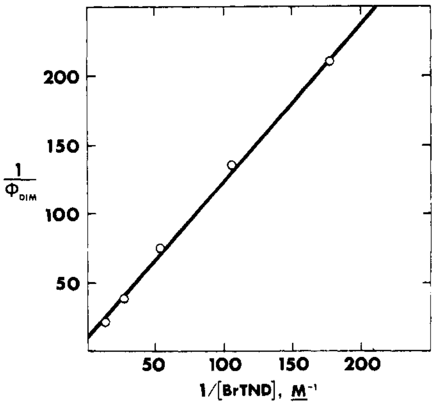


Figure 2. The dependence of ϕ_{DIM} upon different concentrations of BrTND undergoing dimerization at 313 nm in benzene.

Table I. Concentration Dependence for Quantum Yield of TND Dimer Formation in Bromoethane at 313 nm

$\phi_T{}^a$	$1/\phi_T$	$[TND]_{av}$, M	$1/[TND]_{av}$, M^{-1}
0.100	9.97	0.0572	17.5
0.0434	23.0	0.0228	43.8
0.0272	36.7	0.0141	70.9
0.0215	46.5	0.0111	90.1

[a] Mean of three determinations at each concentration.

Table II. Concentration Dependence for Quantum Yield of BrTND Dimer Formation in Benzene

$\phi_{DIM}{}^a$	$1/\phi_{DIM}$	$[BrTND]_{av}$, M	$1/[BrTND]_{av}$, M^{-1}
0.0475	21.0	0.0790	12.6
0.0257	38.9	0.0386	25.9
0.0134	74.6	0.0190	52.6
0.00745	134	0.00943	106
0.00476	210	0.00562	178

[a] Mean of three determinations at each concentration.

solvents of interest in this study.

C. Quenching Studies. The excited triplet state of TND was reported to be the single precursor of all dimers of TND. Since we expected BrTND to behave in a similar fashion, we first studied the concentration quenching of the dimerization of irradiated BrTND with the use of cyclooctatetraene (COT). We had used this quencher successfully in other studies[4d,e] and chose it because its reported triplet energy is about 39 kcal/mol.[10] The estimated triplet energy of TND is 50 ± 1 kcal/mol,[5] and we suspected that the triplet energy of BrTND would be of similar size. Much to our consternation, the Stern-Volmer study of BrTND showed extreme curvature over a wide range of COT concentration (Figure 3, Table III).

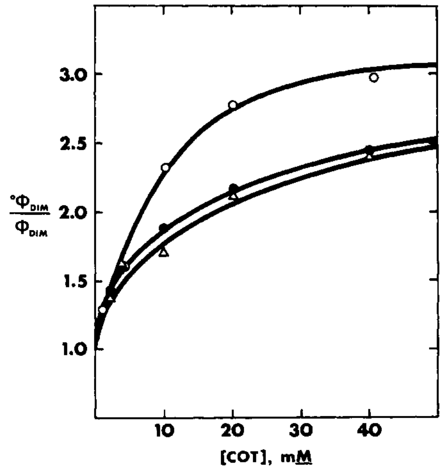


Figure 3. Stern-Volmer plots of the dependence of ϕ_{DIM} as a function of the concentration of cyclooctatetraene (COT) quencher in benzene: (○) 22.4 mM in BrTND, (●) 39.6 mM in BrTND, (△) 61.5 mM in BrTND.

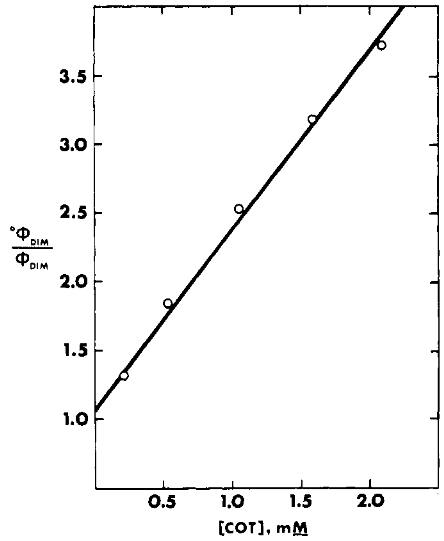


Figure 4. Stern-Volmer plot of the dependence of ϕ_{DIM} of a 23.2 mM TND solution in benzene as a function of cyclooctatetraene (COT) quencher concentration.

Since no quenching studies of TND were reported, we investigated the quenching of the photodimerization of excited triplet TND with COT (Table IV). The variation in quantum yield of TND dimerization with varying concentrations of COT remained linear to about 75% total quenching (Figure 4). Higher concentrations of quencher were not used because of the interference of the weak long-wavelength absorbance of COT at 313 nm.

The photodimerization of BrTND was investigated in the presence of solutions saturated with pure oxygen gas. In the presence of this highly efficient quencher, photodimerization continued but at a reduced rate.

D. Chemical Sensitization and Triplet Energy of 2-Bromothianaphthene 1,1-Dioxide. Irradiation of BrTND at wavelengths greater than 350 nm in a series of benzene solutions of *cis-* and *trans-*1,2-diphenylpropene was performed. The ratio of cis/trans olefin at the photostationary state was found to be 0.263 ± 0.003. This observation is consistent with an excited state triplet energy of ≤44 kcal/mol for BrTND.[11] These olefins were not entirely effective in the quenching formation of the photodimer.

Table III. Quantum Yields of Dimerization of BrTND in the Presence of Cyclooctatetraene (COT) Dissolved in Benzene

$[\mathrm{BrTND}]_{\mathrm{av}}$, mM	$^\circ\phi_{\mathrm{DIM}}/\phi_{\mathrm{DIM}}{}^a$	$^\circ\phi_{\mathrm{T}}/\phi_{\mathrm{T}}$	[COT], mM
22.4	1.29	1.48	1.05
($^\circ\phi_{\mathrm{DIM}} = 0.0164$)	1.41	1.72	2.10
	1.61	2.21	4.19
	2.32	5.63	10.0
	2.78	13.4	20.1
	2.98	25.2	40.6
39.6	1.42	1.82	2.00
($^\circ\phi_{\mathrm{DIM}} = 0.0258$)	1.62	2.40	4.00
	1.87	3.45	10.0
	2.17	5.65	20.0
	2.45	10.4	40.0
61.5	1.38	1.72	2.00
($^\circ\phi_{\mathrm{DIM}} = 0.0350$)	1.64	2.50	4.00
	1.70	2.72	10.0
	2.13	5.42	20.0
	2.40	9.70	40.0

[a] Mean of three determinations at each quencher concentration.

Table IV. Quantum Yields of TND Dimerization in the Presence of Cyclooctatetraene (COT) Dissolved in Bromoethane

$^\circ\phi_{\mathrm{DIM}}/\phi_{\mathrm{DIM}}{}^a$	[COT], mM
1.32	0.209
1.85	0.523
2.52	1.05
3.19	1.57
3.71	2.09

[a] Mean of three determinations at each concentration; $[\mathrm{TND}]_{\mathrm{av}} = 23.2$ mM, $^\circ\phi_{\mathrm{DIM}} = 0.0439$.

Thus, in corroboration of the oxygen and COT quenching studies, the isomerization studies indicate that a separate unquenchable reaction is present.

The data from sensitized diphenylpropene isomerization suggested that the triplet energy of BrTND is very low. We attempted to get a better estimate of the triplet energy by using dye-sensitized photodimerization of BrTND. The choice of sensitizers in this low energy region is quite limited. The two dyes that were used were the crown ether complex of disodium Rose Bengal[4e] (E_{T} = 45 kcal/mol)[12] and crystal violet (E_{T} ~39 kcal/mol)[13] dissolved in acetonitrile. Irradiation of mixtures of these dyes with BrTND using the intense 589-nm light from a sodium vapor lamp for extended periods of time led to the production of the photodimer of BrTND in the Rose Bengal mixture, but none was detectable in the crystal violet mixture. These results suggest that the excited-state triplet energy of BrTND lies in the range $39 < E_{\mathrm{T}} < 44$ kcal/mol. This range of energies also confirms that photodimerization quenching by COT (E_{T} = 39 kcal/mol) is an exothermic process.

The concentration dependence of the dimerization of BrTND sensitized by Michler's ketone at 366 nm was studied in benzene. The data in Table V are plotted in Figure 5, and a linear relation between the reciprocal of the quantum yield of sensitized dimerization and the reciprocal of the concentration of BrTND is found.

E. Luminescence of BrTND. We observed that irradiated samples of benzene solutions of BrTND emitted light. Spectrophotofluorimetric measurements established that BrTND when excited at 320 nm showed emission maxima at 395 and 380 nm in 95% ethanol and cyclohexane, respectively. Addition of COT to an alcohol solution of BrTND showed minor but detectable quenching of fluorescence when the COT/BrTND ratio was 5:1.

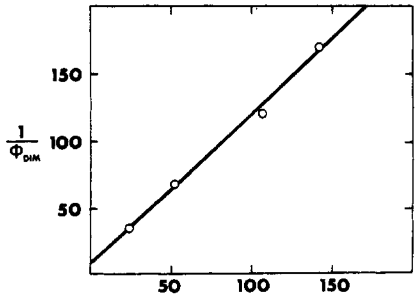


Figure 5. The dependence of ϕ_{DIM} upon different concentrations of BrTND undergoing sensitized dimerization by 2.0 mM Michler's ketone at 366 nm.

Table V. Concentration Dependence for Quantum Yield of Sensitized Formation of BrTND Dimer in Benzene[a]

$\phi_{\mathrm{DIM}}{}^b$	$1/\phi_{\mathrm{DIM}}$	$[\mathrm{BrTND}]_{\mathrm{av}}$, M	$1/[\mathrm{BrTND}]_{\mathrm{av}}$, M^{-1}
0.0296	33.8	0.0438	22.8
0.0149	67.2	0.0193	51.8
0.00830	120	0.00943	106
0.00588	170	0.00709	141

[a] [Michler's ketone] = 2.0 mM. [b] Mean of three determinations at each concentration.

Because the fluorescence emission spectrum of 2-phenylthianaphthene 1,1-dioxide has been quantified[14] and because its absorption spectrum is nearly the same as BrTND, we performed a comparative luminescence study of these two molecules. From this study we estimate that ϕ_{F} for BrTND is 0.011. The 2-phenyl derivative has a ϕ_{F} of 0.74,[14] so that the fluorescence of BrTND is substantially quenched by the presence of the heavy atom.

Discussion

A. External Heavy Atom Effect on Thianaphthene 1,1-Dioxide (TND). The data reported by Harpp and Heitner established that the photodimerization of TND was essentially derived from the excited triplet state of TND attacking the ground state of the same substrate.[5] Our study shows[1b] that the heavy atom solvent bromoethane enhances the quantum yield of dimerization and leads to an intersystem crossing quantum yield of unity. Equation 1 expresses the kinetic form of dimerization of TND[5]

$$\frac{1}{\phi_{\mathrm{DIM}}} = \frac{1}{\alpha\phi_{\mathrm{isc}}} + \frac{k_{\mathrm{d}}}{\alpha\phi_{\mathrm{isc}}k_{\mathrm{r}}[\mathrm{TND}]} \qquad (1)$$

where α is the fraction of intermediate diradicals that produces product, and the parameters k_{d} and k_{r} are respectively the excited triplet-state decay rate constant and the rate constant for excited triplet TND attacking ground state TND. The value α was shown to be unity in TND and the value of ϕ_{isc} for TND in benzene is 0.18.[5] We note that the function describing these data in the solvent bromoethane has an intercept of 1.10 ± 0.12. The ratio $k_{\mathrm{d}}/k_{\mathrm{r}}$ obtained by dividing the slope by the intercept has the value 0.46. Since $\alpha = 1$, the value of the intercept implies that ϕ_{isc} is nearly unity. The ratio $k_{\mathrm{d}}/k_{\mathrm{r}}$ as computed by us from the original data[5] in benzene solution is 0.22. Thus, we find that $\mathrm{T}_1 \leftarrow \mathrm{S}_1$ and $\mathrm{S}_0 \leftarrow \mathrm{T}_1$ are both enhanced by external heavy atom perturbation upon TND. These perturbations appear to follow the general trends found in other molecular systems.[4]

To obtain explicit values for k_{d} and k_{r} it was necessary to study the quenching of the TND reaction by the quencher cyclooctatetraene (COT). The Stern-Volmer relation (eq 2) remained essentially linear to about 75% of total quenching.

$$\frac{(^\circ\phi_{\mathrm{DIM}}/\phi_{\mathrm{DIM}})^{-1}}{[\mathrm{Q}]} = \frac{k_{\mathrm{q}}}{k_{\mathrm{d}} + k_{\mathrm{r}}[\mathrm{TND}]} \qquad (2)$$

The k_d/k_r value from eq 1 is inserted into eq 2 to calculate individual values of k_d and k_r that are dependent only upon the value of k_q chosen. Following the usual assumptions of viscosity-dependent diffusion control for quenching by COT and exothermic energy transfer, values for k_d and k_r are found respectively to be $8.8 \times 10^6\ s^{-1}$ and $1.9 \times 10^7\ M^{-1}\ s^{-1}$ when $k_q = 1.2 \times 10^{10}\ s^{-1}$.

B. Proposed Mechanism for Photodimerization of 2-Bromothianaphthene 1,1-Dioxide. The mechanistic interpretation of the data must explain the following results: (a) photodimerization of BrTND under direct irradiation cannot be completely quenched with any efficient triplet-state quencher; (b) photodimerization of BrTND can be sensitized by known triplet-state sensitizers; and (c) BrTND yields data that produce a curved Stern–Volmer relation when quenched by COT whereas TND treated similarly gives a linear correlation.

To accommodate these seemingly disparate results, we have proposed the multipathway mechanism outlined in Chart I.

Chart I

	Rate	
$S \xrightarrow{h\nu} {}^1S$	Ia	(3)
${}^1S \xrightarrow{k_{ic}} S$	$k_{ic}[{}^1S]$	(4)
${}^1S \xrightarrow{k_f} S + h\nu$	$k_f[{}^1S]$	(5)
${}^1S + S \xrightarrow{k_e} E$	$k_e[{}^1S][S]$	(6)
$E \xrightarrow{k_{-e}} 2S$	$k_{-e}[E]$	(7)
$E \xrightarrow{k_s} \text{dimer}$	$k_s[E]$	(8)
${}^1S \xrightarrow{k_{isc}} {}^3S$	$k_{isc}[{}^1S]$	(9)
${}^3S \xrightarrow{k_d} S$	$k_d[{}^3S]$	(10)
${}^3S + Q \xrightarrow{k_q} S + {}^3Q$	$k_q[{}^3S][Q]$	(11)
${}^3S + S \xrightarrow{k_r} D$	$k_r[{}^3S][S]$	(12)
$D \xrightarrow{k_{-r}} 2S$	$k_{-r}[D]$	(13)
$D \xrightarrow{k_T} \text{dimer}$	$k_T[D]$	(14)

S is substrate BrTND, E is excimer, D is triplet diradical intermediate, and Q is quencher. We define the parameters $\alpha = k_T(k_{-r} + k_T)^{-1}$ and $\beta = k_s(k_{-e} + k_s)^{-1}$ as the respective fractions of triplet diradical intermediate and excimer going on to product. It should be noted that α was shown to equal unity for TND.[5]

Using the steady-state approximation for the solution to these rate equations one obtains for the quantum yield of dimerization of BrTND the expression

$$\phi_{DIM} = \frac{\alpha k_r k_{isc}[S]}{(k_{ic} + k_f + k_{isc} + k_e[S])(k_d + k_r[S] + k_q[Q])} + \frac{\beta k_e[S]}{(k_{ic} + k_f + k_{isc} + k_e[S])} \qquad (15)$$

The first term in eq 15 represents the quantum yield of dimerization of BrTND from excited triplet (ϕ_T) and the second term in the equation represents the quantum yield of dimerization from excited singlet (ϕ_S). The reciprocal of ϕ_S is defined as

$$\frac{1}{\phi_S} = \frac{1}{\beta} + \frac{k_{ic} + k_f + k_{isc}}{\beta k_e[S]} \qquad (16)$$

Similarly, when $[Q] = 0$, ϕ_T may be expressed as

Table VI. Evaluation of Data for BrTND Dimerization

Concentration Dependence, ϕ_{DIM}

[Michler's ketone], mM	0	2.0
Slope, M	1.14 ± 0.03	1.13 ± 0.02
Intercept	10.4 ± 3.0	7.4 ± 2.2
Correlation coefficient	0.999	0.998

COT Dependence

$[BrTND]_{av}$, mM	22.4	39.6	61.5
Asymptote	3.24	2.90	2.86
Linearization:			
Slope, M^{-1}	612 ± 19	227 ± 6	212 ± 11
Intercept	0.42 ± 0.34	1.24 ± 0.11	1.16 ± 0.21
Correlation coefficient	0.998	0.999	0.994

Concentration Dependence, ϕ_S		Derived Quantities	
Slope, M^{-1}	4.1 ± 0.2	α	0.14
Intercept	12 ± 7	β	0.08
Correlation coefficient	0.998	k_r	$(2.2 \pm 0.9) \times 10^8\ M^{-1}\ s^{-1}$
		k_d	$(3.3 \pm 1.4) \times 10^7\ s^{-1}$
		ϕ_{isc}	0.39 ± 0.2

$$\frac{1}{\phi_T} = \frac{1}{\alpha\phi_{isc}} + \frac{k_d}{\alpha\phi_{isc}k_r[S]} \qquad (17)$$

where ϕ_{isc}, the intersystem crossing quantum yield, is the usual expression:

$$\phi_{isc} = \frac{k_{isc}}{k_{ic} + k_f + k_{isc} + k_e[S]} \qquad (18)$$

Similar mechanisms were proposed in studies of the photodimerization of acenaphthylene[4a,15] and coumarin.[16] The present scheme does not take into account the possibility that a singlet excimer could intersystem cross to form a triplet excimer, a process detected in the fluorescence quenching of naphthalene in the presence of *trans*-β-ethylstyrene.[17]

Because from BrTND a single photodimer is produced regardless of the history of the excited state preceding its formation, there is no direct way to measure the amount of excimer-derived product when all triplet monomers of BrTND are quenched. We suggest that alternative mechanistic schemes can be derived, such as excitation of a ground-state complex, but the important fact to be explained is the unquenchable portion of this reaction.

C. The Triplet State. Data from the Michler's ketone sensitized dimerization of BrTND in benzene solvent allows direct evaluation of α and the ratio k_d/k_r by use of eq 17 because ϕ_{isc} is unity for Michler's ketone[18] and the excimer mechanism is absent. Thus, ϕ_{DIM} now equals ϕ_T where all products are triplet derived.

In Table VI are enumerated all the derived constants for BrTND. We note that α for BrTND is 0.14, which means that about 14% of all triplet derived diradicals proceed to product. This is in sharp contrast to TND, whose value for $\alpha = 1$.[5] We suggest that the source of this inefficiency in BrTND is increased steric hindrance to ring closure of the intermediate diradical. The addition of two bulky bromine groups at the reaction site must increase the transition state energy for ring closing compared to the TND diradical intermediate and as a consequence disproportionation of the BrTND intermediate becomes very competitive with cyclization. Previous evidence suggests that steric effects can inhibit photodimerization of TND derivatives. Mustafa and Zayed reported that under long-term irradiation 2-methylthianaphthene 1,1-dioxide produced photodimer but the 2,3-dimethyl derivative remained inert to irradiation.[19]

D. Nonlinear Stern–Volmer Behavior. The nonlinear behavior of COT quenching of photodimerization of BrTND in benzene was investigated at three different substrate con-

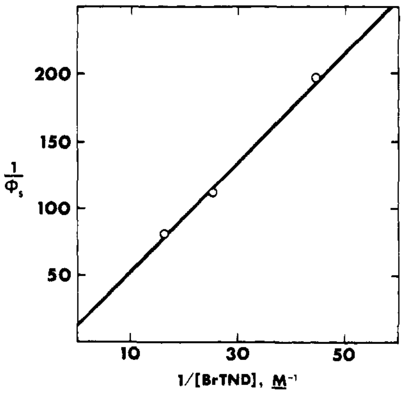


Figure 6. The dependence of ϕ_S upon different concentrations of BrTND undergoing dimerization in benzene.

centrations of BrTND as illustrated in Table III. The data describe functions that asymptotically approach limiting values for $°\phi_{DIM}/\phi_{DIM}$ (Figure 3). These data suggest the deduction that over the investigated range of BrTND concentrations, up to 31% of photoproduct does not arise from triplet BrTND.

Curved Stern-Volmer plots are not uncommon and theoretical discussions have been put forward.[20] We have chosen a mathematical approximation that allows us to obtain derived values of most of the rate constants in eq 15.

In the Stern-Volmer treatment we define the limit of the asymptotic value of each curve as $°\phi_{DIM}/\phi_{DIM} = °\phi_{DIM}/\phi_S$, where ϕ_S is the quantum yield of dimer formation from unquenchable excimer.[20] Each curve represents the quenching by COT of a different fixed BrTND concentration. Thus, we assume that at the asymptotic limit of quenching we have achieved an approximate measure of the quantum yield, ϕ_S, at the given initial concentration of BrTND.

Because from eq 15

$$\phi_{DIM} = \phi_T + \phi_S \qquad (19)$$

we can define the following Stern-Volmer equation:

$$\frac{°\phi_{DIM} - \phi_S}{\phi_{DIM} - \phi_S} = \frac{°\phi_T}{\phi_T} = 1 + \frac{k_q[Q]}{k_d + k_r[S]} \qquad (20)$$

This equation can be plotted if ϕ_S is known. We have determined ϕ_S by asymptotic approximation at three different concentrations of BrTND. From eq 16 a plot of ϕ_S^{-1} vs. $[S]_{av}^{-1}$ yields a *linear correlation* (Figure 6). This relationship allows us to make reasonable estimates of the value of ϕ_S at any concentration of S within the range of values studied.

Data from the sensitized dimerization of BrTND have made available the values of α and the ratio k_d/k_r, since $k_e[S] = 0$ and $\phi_{DIM} = \phi_T$ in this case. Using eq 16 to evaluate ϕ_S at each concentration of BrTND where ϕ_{DIM} is known, we can introduce values of ϕ_T and ϕ_S into the Stern-Volmer eq 19 and obtain reasonable estimates of the rate constants.

Assuming that quenching of BrTND by COT is diffusion controlled, the estimate of k_q for COT in benzene of 1.2×10^{10} M^{-1} s^{-1} is obtained from the well-known viscosity formula.[22] From the linearized Stern-Volmer plots, values (Figure 7) of the function ($k_d + k_r$[S]) can be computed and combined with the known ratio of k_d/k_r to get the individual results for each rate constant. Considering the errors inherent in such a treatment, we feel that the data in Table VI are reasonable approximations.

We note that the values of k_d and k_r both are larger for BrTND dissolved in benzene as compared to TND dissolved in bromoethane. The observation that the internal heavy atom has a greater perturbation on $k_d(S_0 \leftarrow T_1)$ than does the external heavy atom is consonant with prior studies.[1,4]

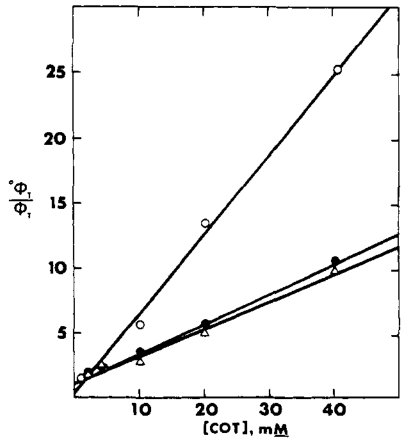


Figure 7. The dependence of the linearized Stern-Volmer plots of ϕ_T as a function of the concentration of cyclooctatetraene (COT) in benzene: (○) 22.4 mM in BrTND, (●) 39.6 mM in BrTND, (△) 61.5 mM in BrTND.

Table VII. *Concentration Dependence for ϕ_T of BrTND Dimer Formation in Benzene*

ϕ_S	ϕ_T	$1/\phi_T$	$[BrTND]_{av}$, M	$1/[BrTND]_{av}$, M^{-1}
0.0156	0.0319	31.3	0.0790	12.6
0.00846	0.0172	58.0	0.0386	25.9
0.00439	0.00901	111	0.0190	52.6
0.00224	0.00521	192	0.00943	106
0.00135	0.00341	293	0.00562	178

The increase in k_r by about a factor of 10 in BrTND compared to TND is less readily interpreted. Harpp and Heitner proposed a *transition* state that was polar,[5] and it may be that the bromo substituent further enhances this polarity with a concomitant increase in the rate of formation of the diradical intermediate.

From eq 16 we observe that the intercept of a graphical plot of the data leads to a value of β, the fraction of excimer going on to product. From the slope of the plot of eq 16 a comparison to other constants of k_e, the rate constant for formation of exciplex, can be made. Thus the value of β of about 0.08 suggests that relatively few exciplexes form dimer. The decay of the excimer back to ground state, therefore, becomes another energy-wasting step in the photochemical dimerization of BrTND. Evaluating the slope we find that the following relation holds

$$0.3k_e \simeq k_{ic} + k_f + k_{isc}$$

Thus, the exciplex has a rate constant of formation significantly larger than the other processes in competition with it. However, the exciplex also inefficiently forms product, and we feel that steric effects must be a major factor in inhibiting dimer formation from the exciplex.

E. Evaluation of ϕ_{isc}. The estimate of ϕ_{isc} in BrTND is dependent on the variation of ϕ_T with the concentration of BrTND. The value of ϕ_T is indirectly obtained from values of ϕ_S and the use of eq 19. Since direct irradiation produces values for ϕ_{DIM}, values of ϕ_T are calculated and then used in eq 17 to produce the data of Table VII and the corresponding plot in Figure 8. These data describe a linear relation (correlation coefficient = 0.998) with a slope of 1.57 ± 0.06 and an intercept corresponding to ($1/\alpha\ \phi_{isc}$) of 19 ± 6. Since $\alpha = 0.14$, this suggests that ϕ_{isc} is 0.39 ± 0.2. This value is not as high as might be expected. However, BrTND

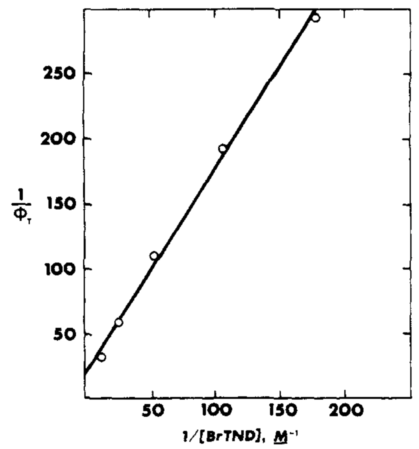


Figure 8. The dependence of ϕ_T upon different concentrations of BrTND undergoing dimerization in benzene.

does exhibit some fluorescence, and this suggests that our estimate for ϕ_{isc} is reasonable especially when the complications of the quenching data are considered.

Summary

The results clearly corroborate the fact that TND photodimerizes by attack of excited triplet TND upon ground-state TND. In contrast, BrTND dimerizes inefficiently by two different mechanistic pathways that we have interpreted as attack of excited triplet BrTND upon ground-state BrTND and through exciplex formation. Both pathways show poor efficiency in forming product, and we interpret this to suggest that the steric bulk of bromine may interfere dramatically with the final step of ring closing.

The dichotomy between the mechanism of photodimerization of TND and BrTND has no ready explanation. An important factor contributing to the formation of exciplexes is considered to be dipolar charge distribution.[23] We assume that the 2-bromo substituent enhances charge polarity in the excited state and thus causes an exciplex to form in competition with photodimerization.

As a referee has commented, the assumption of a trans dimer arising from an excimer is unusual because the known arene excimer processes produce cis dimers.[16,24] We were concerned with this enigma when it became apparent early in our studies that no cis dimer could be found.

We suggest that the steric bulk of BrTND precludes such "maximum overlap" products. If the excited state of BrTND is highly localized at the 2,3-double bond, then the π-bonds could form an excimer that demands no participation from the benzene ring. We can only presume that similar mechanisms in other systems will eventually be found.[25]

It is of particular interest to note that the external heavy atom seems to be more efficient in enhancing the ($T_1 \leftarrow S_1$) transition in TND ($\phi_{isc} \sim 1$) than the bromo substituent placed at the 2 position of TND ($\phi_{isc} = 0.4 \pm 0.2$). This difference may be due to experimental error introduced by the approximations required to linearize the quenching data for BrTND. On the assumption that it is, in fact, a real difference, the explanation may be related to the large formation rate constant for the exciplex which competes with the rate of intersystem crossing.

It will be of interest to see if molecular orbital calculations indicate that spin-orbital coupling at the 2 position is reduced. If so, this would be another contributing factor to the decrease in efficiency of the internal heavy atom in 2-bromothianaphthene 1,1-dioxide.

Experimental Section

Materials. Thianaphthene 1,1-dioxide (TND) was prepared as previously described[26] and purified by recrystallization from absolute ethanol and dried. 2-Bromothianaphthene 1,1-dioxide (BrTND) was prepared as previously described,[27] recrystallized from absolute ethanol, and dried. 2-Phenylthianaphthene 1,1-dioxide was prepared as previously described,[28] recrystallized twice from 95% ethanol with activated charcoal decolorization, and dried.

The crown ether complex of Bengal Red B was available from a previous study.[4e] Crystal violet (Fisher) and 9-fluorenone (Aldrich) were used without further purification. Benzophenone (Eastman) was recrystallized from absolute ethanol. Michler's ketone (Eastman Practical) was eluted with chloroform through a 2.5 × 60 cm column of alumina and the eluate residue recrystallized from absolute ethanol and dried.

Cyclooctatetraene (ChemSampCo) was passed through a short alumina column before use. 1,3-Cyclohexadiene (Aldrich) was used without further purification. Benzene and cyclohexane (Eastman Spectrograde) were freshly distilled from CaH_2 before use. Ethyl bromide (Aldrich) was freshly distilled before use. Acetonitrile (Aldrich) was distilled from P_4O_{10} before use.

Instrumentation. GLC analyses were performed using a 5 ft × ⅛ in. column of 1.5% OV-101 on Chromosorb G on either a Varian 1200 or 2400 Hy-FI with a Sargent SR recorder equipped with a ball-disc integrator. Ultraviolet measurements were obtained from a Beckman DB-G recording spectrophotometer. Precise quantum yield determinations were obtained using a Bausch and Lomb 33-86-07 grating monochromator with 150-W xenon lamp. Infrared spectra were obtained as thin films on NaCl plates or in KBr pellets on a Perkin-Elmer 337 spectrometer. Emission spectra were determined on an Aminco-Bowman spectrophotofluorimeter. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Irradiations. General. Preparative irradiations and quenching studies were carried out in a Rayonet RPR-100 reactor fitted with lamps emitting light in the 3500-Å region. Photolysis tubes were suspended in the reactor by means of a MGR-100 merry-go-round apparatus.

Direct irradiations for concentration studies were performed with a Hanovia 450-W mercury-arc lamp and Corex sleeve placed in a quartz immersion well through which cold K_2CrO_4-K_2CO_3 solution was circulated to isolate the light output around 313 nm.[5] This combination was centered in a Rayonet MGR-500 merry-go-round apparatus and housed in a box designed to keep out stray light.

Sensitization studies were carried out with the lamp placed in a Pyrex immersion well through which cold 0.7 M $Cu(NO_3)_2$ solution was circulated. Corning CS-7-60 filters were placed around the immersion well[29] so that a band of light between 360 and 390 nm was transmitted. Sensitized irradiations of BrTND at 589 nm were performed as in a previous study.[4e]

Vycor test tubes (15 × 125 mm) calibrated to contain 10 ml were filled with the solutions to be irradiated, and each tube was sealed with a rubber syringe cap. Oxygen was removed by a 15-min purge with nitrogen. Actinometer solutions were irradiated in parallel with the reaction mixtures. All nonpreparative runs were carried out to low (<15%) conversions of reactant. After irradiation was terminated, the amount of unreacted BrTND was determined by quantitative spectrophotometric analysis using previously determined extinction coefficients. Representative quantum yields were confirmed with determinations made on a Bausch and Lomb monochromator at 313 ± 10 nm.

Actinometry. The benzophenone-sensitized dimerization of 1,3-cyclohexadiene at 313 and 366 nm[30] was used as the actinometer with n-tetradecane (Baker) as internal standard. Actinometer solutions were analyzed on either a 4 ft × ⅛ in. column of 3% OV-1 on Chromosorb W or a 5 ft × ⅛ in. column of 1.5% OV-101 on Chromosorb G.

Beer-Lambert Studies of TND and BrTND. Spectrophotometric analyses were made of the absorbance (A) of a 0.0241 M solution of TND and its two- and fourfold dilutions at 304 nm in a series of solvents. Least-squares analyses of the absorbance data indicate the following: (solvent, molar extinction coefficient, A_∞) ethyl bromide, $(2.42 \pm 0.01) \times 10^3$, 0.004 ± 0.002; methanol, $(2.18 \pm 0.03) \times 10^3$, 0.002 ± 0.004; benzene, $(2.34 \pm 0.01) \times 10^3$ (lit.[5] $(2.32 \pm 0.061) \times$

10^3), 0.001 ± 0.002.

Spectrophotometric analysis was made of the absorbance (A) of a 0.0204 M solution of BrTND and its two- and fourfold dilutions at 322 nm (uv max) in benzene. Least-squares analysis of the absorbance data indicated a molar absorptivity (ϵ) of $(4.44 \pm 0.03) \times 10^3$ and A_∞ of 0.002 ± 0.004.

Preparative Dimerization of BrTND. Ten Vycor test tubes filled with 10 ml of 0.0450 M BrTND in benzene were irradiated until uv analysis of the reaction mixture indicated <10% of unreacted starting material remained. The photolysate solutions were decanted from the crystalline photoproduct coating the test tube walls. Solvent was removed from the combined benzene solutions to afford a tan solid that was triturated with methanol to remove the unreacted starting material (70 mg, 6.3%) of BrTND recovered by recrystallization from ethanol. Infrared analysis showed no detectable difference between the solution residue and crystalline product; combined recovery of crude photoproduct was 1.03 g (93%). Recrystallization from Me_2SO with charcoal decolorization afforded 663 mg of colorless dimer, mp 366 °C dec (lit.[19] mp 360 °C); ir 3080, 2940, 1311, 1180, 1151, 1128, 1062, 941, 782, 754, 698, and 602 cm^{-1}; mass spectrum, 70 ev, m/e (relative intensity) 492 (1), 490 (2), 489 (1), 488 (0.1), 411 (7), 409 (7), 303 (7), 301 (12), 246 (50), 244 (49), 237 (13), 221 (10), 202 (22), 200 (22), 165 (20), 137 (100), 109 (43), 101 (25), and 100 (23). Anal. Calcd for $C_{16}H_{10}Br_2O_4S_2$: C, 39.20; H, 2.06; Br, 32.60; S, 13.08. Found: C, 39.35; H, 2.15; Br, 32.33; S, 13.23.

Reduction of Photodimer of BrTND. Into a three-necked, 100-ml round-bottom flask charged with 495 mg (13 mmol) of $LiAlH_4$, 30 ml of diglyme previously stored over sodium was distilled from $LiAlH_4$, under nitrogen. To the stirred $LiAlH_4$ suspension, 1.00 g (2.04 mmol) of crude dimer was added and the stirred mixture heated at reflux for 150 min. The reaction after cooling was quenched with 1 ml of 10% aqueous NaOH followed by 1 ml of water. After removal of solvent by vacuum distillation, the crude reaction residue was triturated with hot chloroform to separate the product from inorganic salts. Evaporation of the chloroform extracts afforded 620 mg (91%) of crude product, whose ir spectrum was found to be identical with that of authentic TND photodimer.[31] Comparison with the ir spectrum of mixed TND photodimers confirmed the absence of the head-to-head isomer. Recrystallization of the reduction product from Me_2SO afforded pure TND dimer, mp 337.0–338.5 °C (lit.[5] mp 334–335 °C dec).

Dimerization of BrTND in the Presence of Oxygen. A 15 × 125 mm Pyrex test tube was charged with 10 ml of a benzene solution which was 50 mM in BrTND. The tube was sealed with a rubber syringe cap and a stream of oxygen passed through the solution for 30 min. Workup of the photolysate after irradiation at 3500 Å for 18 h afforded 44 mg (35%) of crude crystalline photodimer whose physical properties were identical with those of BrTND dimers.

Quantum Efficiency of BrTND Fluorescence. Fluorescence emission in cyclohexane was measured for a 94 μM solution of 2-PhTND ($\phi_f = 0.74$) and a 220 μM solution of BrTND. Spectra were corrected for instrument response[32] and relative incident light absorbance. Comparison of the relative areas under the corrected emission curves indicated $\phi_f = 0.011$ for BrTND.

***trans*-1,2-Diphenylpropene** was obtained in 75% yield by the acid-catalyzed dehydration of 1,2-diphenylpropan-2-ol[33] (bp 102–107 °C (0.15 Torr), mp 47.5–48.5 °C). Two recrystallizations of crude product from ethanol afforded colorless plates, mp 81.5–82.5 °C (lit.[34] mp 82–83 °C), which GLC analysis indicated contained <0.5% of the cis isomer.

***cis*-1,2-Diphenylpropene.** A 500-ml capacity photolysis vessel was charged with 5.00 g (25.7 mmol) of *trans*-1,2-diphenylpropene and 4.50 g (25 mmol) of 9-fluorenone. Benzene was distilled into the vessel from CaH_2 and the solution was centered in a Rayonet photochemical reactor and fitted with a reflux condenser and nitrogen inlet. The solution was then irradiated at 3500 Å under nitrogen for 40 h, at which time GLC analysis indicated a cis/trans isomer ratio of 9. After an additional 24 h of irradiation the product ratio had increased to 10.

Removal of solvent from the photolysate afforded a solid residue which was taken up in 50 ml of methanol containing 0.50 g (13 mmol) of $NaBH_4$. After 1 h of reflux, the reaction mixture was partitioned between water and hexane. The hexane layer was dried over Na_2SO_4, the solvent removed, and the crude mixture of 9-fluorenol and olefins eluted with hexane through a 3 × 50 cm column of alumina. The first 300 ml of eluate contained essentially pure cis isomer which was recrystallized from methanol to afford 3.02 g (67%) of *cis*-1,2-diphenylpropene as colorless needles, mp 46–47 °C (lit.[34] mp 48 °C), which was shown by GLC analysis to contain <0.5% of the trans isomer.

Table VIII. Isomer Composition of 1,2-Diphenylpropenes

Solution	Cis/trans Initial	Cis/trans Final
1	4.20	0.270
2	1.99	0.263
3	1.01	0.267
4	0.520	0.261

Isomerization of 1,2-Diphenylpropenes in the Presence of BrTND. Nitrogen-degassed benzene solutions 50 mM in both BrTND and 1,2-diphenylpropene were irradiated at 3500 Å for 15 h. The *cis-/trans*-1,2-diphenylpropene ratios as determined by GLC analysis are summarized in Table VIII.

Dye-Sensitized Dimerization of BrTND. Two test tubes containing nitrogen-degassed acetonitrile solutions 50 mM in BrTND and respectively 0.8 mM in disodium bis(dicyclohexyl-18-crown-6)-Bengal Red B complex and 0.5 mM in crystal violet were irradiated at 589 nm for 24 h. Workup of the Bengal Red sensitized photolysate afforded 42 mg (29%) of crude photodimer, whereas no photodimer in addition to unreacted BrTND was detected in the solution containing crystal violet.

Preparative Dimerization of BrTND in Nitromethane. A mixture of BrTND (0.20 g, 0.825 mmol) and 15 ml of freshly distilled nitromethane was purged with dry nitrogen gas for 30 min and then sealed and irradiated at 350 nm in the Rayonet reactor for a period of 42 h. The hard cubes that crystallized on the inside of the tube were collected by suction filtration, air-dried, and weighed to give 30 mg of dimer, mp 366 °C dec, identical in all respects with that obtained from benzene irradiations.

The filtrate was rotary evaporated to dryness and the pale yellow residue dissolved in 50 ml of boiling methanol. Upon cooling to −10° a crop of crystalline cubes formed. These were collected by suction filtration to give 10 mg of a new photodimer. This dimer was recrystallized from a mixture of 7 ml of methanol and 3 ml of nitromethane to produce about 6 mg of cubes, mp 272–276 °C dec: ir 3080 (w), 3060 (w), 2950 (w), 1600 (w), 1450 (w), 1330 (s), 1235 (w), 1188 (sh), 1165 (s), 1138 (s), 1065 (m), 948 (w), 762 (s), 733 (w), 708 (m), 620 (w), 605 (s), 589 (w), 563 (m), 550 (s), 535 (sh), and 505 (m) cm^{-1}; NMR ($CDCl_3$ slurry) δ 5.05 (2 H, methine) and 7.2–7.8 (8 H, Ar). Anal. Calcd for $C_{16}H_{10}Br_2O_4S_2$: C, 39.20; H, 2.06; Br, 32.60; S, 13.08. Found: C, 39.04; H, 1.96; S, 12.98; no Br analysis performed. Evaporation of the original methanol mother liquor to 5 ml followed by cooling to −10° deposited a crop of unreacted BrTND, wt 130 mg.

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Photocyclization of Diethylstilbestrol. Isolation of a Stable, Self-Trapping Dihydrophenanthrene Intermediate

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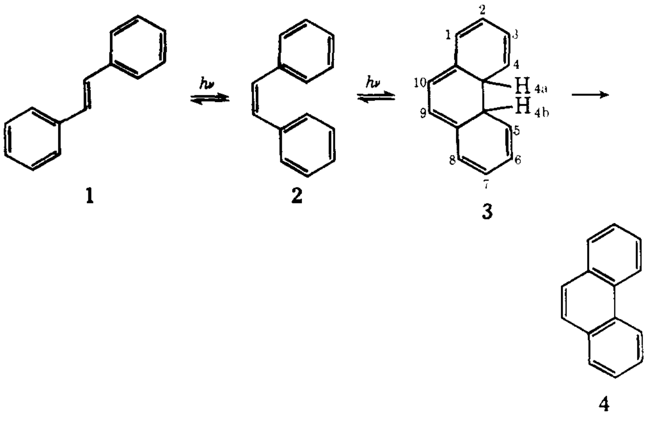
Abstract: Near-ultraviolet irradiation of the synthetic estrogen diethylstilbestrol, a stilbene derivative, resulted in the isolation of the first stable 4a,4b-dihydrophenanthrene. The stability of this DHP is the result of a double tautomerism of the initially formed dienol to a diketone structure in which the tendency to rearomatization is lost. Furthermore, the reverse ring-opening photoreaction may be prevented by the conversion of the prerequisite π,π^* character of the lowest excited singlet to an n,π^* state in the diketone. NMR and mass spectral data provided direct spectrochemical evidence for the trans configuration of the intact 4a,4b-hydrogen atoms, in agreement with orbital symmetry considerations and with recent chemical proof. Time-lapse spectrometric determinations demonstrated the overall transformation to be free of side reactions and to give quantitative conversion to the DHP without further oxidation to the phenanthrene product characteristic of stilbene photocyclizations. The mechanism involves an initial trans ⇌ cis photoisomerization, competitive photocyclization of the cis isomer, and a fast dark tautomerization of the dienol DHP to the isolable dihydrophenanthrenedione product.



Although the photooxidative cyclization of stilbenes (**1**) to phenanthrenes (**4**) is a reaction of remarkable generality and synthetic utility,[2] definitive mechanistic studies have been thwarted by the extreme instability of the proposed intermediate dihydrophenanthrenes (DHP's). These intermediates may often be detected in solution by their visible absorption in the 400–500-nm region, but have heretofore resisted isolation because of rapid oxidative hydrogen abstraction to phenanthrenes or reverse ring opening to starting stilbenes, processes which occur both thermally and photochemically.

Several ingenious, partially successful attempts to prepare stable intermediates have been reported. Muszkat and Fischer[3] photolyzed a hexamethylstilbene to obtain in situ 21% conversion to a "DHP" in which both inner hydrogens were replaced by methyl; the intermediate resisted oxidation but underwent the usual ring opening during attempts at isolation. The same authors achieved 67% conversion in solution upon monochromatic irradiation of fused *cis*-stilbene. Analogous results have been reported by Ramey and Boekelheide.[4] Blackburn et al.[5] reasoned from steric arguments that DHP's prepared from styrylnaphthalenes might have enhanced stability. Their intermediates proved relatively long lived in solution, but were not isolable. Isolation of rearranged, biphenylic, nonoxidized intermediates was described by Sargent and Timmons,[6] but these compounds lacked the true DHP structure, which is characterized by and is chiefly remarkable for the presence of "inner" hydrogens at the 4a,4b positions of the phenanthrene nucleus.

We report the isolation in high yield of a completely stable, true DHP intermediate, obtained upon irradiation of synthetic estrogenic hormone diethylstilbestrol (α,α'-diethyl-4,4'-stilbenediol, DES).[7] Stabilization of this DHP is conferred by a unique self-trapping double enol → keto tau-