Pulse Radiolysis Study of the Cycloheptatriene Triplet State: Lifetime, Relaxation, and "Nonvertical" Excitation

A. A. Gorman,* I. Hamblett, M. Irvine, P. Raby, M. C. Standen, and S. Yeates

Contribution from the Chemistry Department, University of Manchester, Manchester M13 9PL, United Kingdom. *Received July 23, 1984*

Abstract: The triplet state of cycloheptatriene (CHT) has been produced by pulse radiolysis in toluene. Its lifetime of 6 ± 1 μs is considerably longer than for acyclic trienes, ~300 ns, despite a smaller energy gap between the relaxed T_1 and S_0 surfaces. It is proposed that relaxation is from the boatlike spectroscopic state to an approximately planar species within which spin–orbit coupling factors are minimized. Plots of log k_{et} vs. donor triplet energy for endothermic triplet energy transfer to both CHT and the acyclic neo-alloocimene (NA) show that, whereas the latter is close to being a vertical acceptor of triplet energy, CHT exhibits clear "nonvertical" character. In this respect, NA and CHT mimic *trans*- and *cis*-stilbene, respectively. It would appear that, for olefinic systems, *established* "nonvertical" behavior is currently restricted to nonplanar π systems, and the possibility is raised that such behavior may, at least in part, reflect higher vibrational level densities in such systems.

1. Introduction

We have recently described pulse radiolysis experiments which have allowed determination of triplet lifetimes, triplet–triplet absorption spectra, and, in some cases, the relaxed triplet energies of simple conjugated olefinic systems,[1] all of which have been essentially planar in the ground state. In this paper, we report the characterization of the triplet state and the energy-accepting and -donating properties of a conjugated olefin which is nonplanar in the ground state, namely 1,3,5-cycloheptatriene (CHT; **1**). Our

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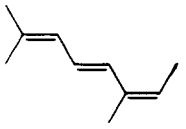

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principal findings are that (a) ^{3}CHT* has a much longer lifetime than typical acyclic trienes, (b) the change in "available" triplet energy on relaxation of the spectroscopic triplet is of the order of 17–18 kcal mol^{-1}, much greater than values for acyclic trienes, and (c) CHT is clearly a "nonvertical" acceptor of triplet energy in the endothermic situation.

In the experiments to be described, we have used the pulse radiolysis technique to populate in toluene the triplet manifolds of (a) CHT both alone and in the presence of triplet energy accepting monitors (M) and (b) monitor molecules (M) in the presence of CHT. Corresponding experiments, where required for comparative purposes, have been carried out with the acyclic triene neo-alloocimene (NA; **2**) whose triplet state has been fully characterized.[1c,d] Our approach has been described in detail elsewhere.[1,2]

2. Experimental Section

Time-resolved work was performed at the Christie Hospital and Holt Radium Institute, Manchester. Pulse radiolysis experiments were carried out with the Vickers 10-MeV linear accelerator with pulse widths of 10 or 20 ns. Details of the updated detection system have been described.[1c] Pulsed laser experiments were performed with a J. K. Lasers System 2000 Nd:YAG laser, pulse width ~12 ns. Voltage wave forms at the anode of a Hamamatsu R928 photomultiplier coupled to a 50-Ω load resistance, rise time < 1 ns, were analyzed as previously described.[1c] Error limits for quoted rate constants are ±10%.

Toluene (AnalaR, BDH) was refluxed over lithium aluminum hydride for 48 h and fractionally distilled. Biphenyl (MeOH–H_2O), naphthalene (EtOH), chrysene (C_6H_6), fluoranthene (EtOH), pyrene (EtOH), anthracene ($C_6H_5CH_3$), perylene ($C_6H_5CH_3$), and β-carotene ($C_6H_5CH_3$–MeOH) were recrystallized. Fluorene was zone-refined. Methylene iodide (Koch-Light) was dried over calcium chloride and fractionated twice from copper powder. Neo-alloocimene (Fluka, 99%) was fractionated under nitrogen at reduced pressure. Cycloheptatriene (Fluka, 98%) retained a persistent pale yellow color after fractionation following a host of conventional purification procedures. Pure colorless material was obtained as follows. (a) Distilled commercial cycloheptatriene (30 g) was converted according to the method of Conrow[3] to the tropylium tetrafluoroborate salt (25 g, 43%). (b) A solution of tropylium tetrafluoroborate (11 g) in water (165 mL) was added dropwise over a period of 0.5 h to a stirred solution of sodium borohydride (4 g) in water (160 mL) in a three-necked flask immersed in an ice bath and fitted with a reflux condenser. The latter was sufficient protection to prevent loss of cycloheptatriene in the hydrogen stream resulting from the $NaBH_4/H_2O$ reaction. This was checked by passing the issuing gas through an acetone/CO_2 trap. After the addition, the pale yellow organic layer was taken up in ether (4 × 50 mL) and dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure at room temperature and fractionation under nitrogen gave pure colorless cycloheptatriene, bp 116 °C (4.0 g, 70%). This material, characterized by ^{1}H NMR, mass, and IR spectroscopy, was homogeneous by GLC (1% Dexsil 300 on Chromosorb W HP, 80–100 mesh; 1.7 m × 4 mm (i.d.); 20 psi, 80 °C).

3. Results

3.1. Detection of ^{3}CHT*. Pulse radiolysis of a deaerated solution of CHT (~2 × 10^{-2} mol L^{-1}) in toluene (T) resulted in "immediate" formation of a transient species, λ_{max} 320 nm (Figure 1), which has been identified as ^{3}CHT* (vide infra). The for-

$$T \xrightarrow{e} {}^1T^*, {}^3T^* \quad (1)$$

$$^3T^* + CHT \rightarrow T + {}^3CHT^* \quad (2)$$

$$^3CHT^* + CHT \rightarrow \text{loss of } {}^3CHT^* \quad (3)$$

$$^3CHT^* \xrightarrow{k_d} CHT \quad (4)$$

mation of this species via channels 1 and 2[1,2,4] was followed by exponential decay (1.4 × 10^5 s^{-1}; Figure 1) which was insensitive to CHT concentration. Thus, self-quenching, channel 3, is unimportant and natural decay in toluene (eq 4) corresponds to a lifetime of 7 μs. This is to be compared with the much smaller value of 333 ns for the triplet state of NA.[1c]

As can be seen in Figure 1, there is an additional long-lived component to the transient decay at 320 nm. Control experiments have shown that this species is solvent-derived and unaffected by

(1) (a) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1981**, *103*, 4553. (b) *J. Photochem.* **1982**, *19*, 89. (c) Gorman, A. A.; Hamblett, I. *Chem. Phys. Lett.* **1983**, *97*, 422. (d) Gorman, A. A.; Hamblett, I.; Jensen, N.-H. *Ibid.* **1984**, *111*, 293.

(2) (a) Craig, B. B.; Gorman, A. A.; Hamblett, I.; Kerr, C. W. *Rad. Phys. Chem.* **1984**, *23*, 111. (b) Gorman, A. A.; Hamblett, I.; Harrison, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6952.

(3) Conrow, K. *Org. Synth.* **1963**, *43*, 101.

(4) One would expect that, as for olefins in general, any ^{1}CHT* produced would not undergo intersystem crossing. Support for this expectation came from experiments involving pulsed laser excitation (265 nm; up to 60 mJ per pulse) of CHT (OD_{265} = 0.5) in cyclohexane. No transient absorption was detected.

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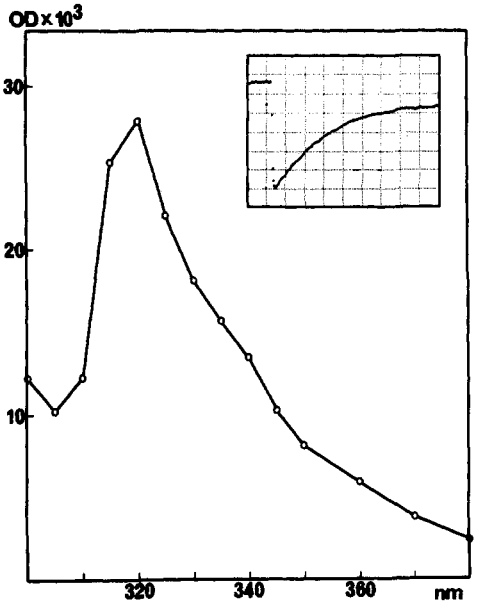


Figure 1. Transient absorption spectrum, 2 μs after absorption of a 20-ns electron pulse by liquid toluene containing CHT (1.9×10^{-2} mol L^{-1}). Inset: Time dependence of corresponding transient decay monitored at 320 nm; 1.4% absorption/division, 2 μs/division.

the presence of oxygen. In contrast, the transient assigned as ^{3}CHT* decayed in aerated toluene with a first-order constant, $k' = 5.6 \times 10^6$ s^{-1}, which indicates a quenching rate constant of 2.7×10^9 L mol^{-1} s^{-1}, assuming an oxygen concentration of 2.0×10^{-3} mol L^{-1} for the aerated solvent.[5] This value is typical of triplet states in general,[6] but larger values ($6–9 \times 10^9$ L mol^{-1} s^{-1}) have been reported,[7] for example, for stilbenes and related molecules where the S_0–T_1 energy gap at the equilibrium T_1 geometry is less than the electronic excitation requirement to form singlet oxygen, $^1\Delta_g$, and the spin-exchange mechanism is particularly favorable.[8]

It has been observed empirically[9] that a linear relationship exists between the absorption maxima of the singlet–singlet and triplet–triplet transitions of retinal and related polyenes, and we have found that the corresponding data for a series of acyclic and monocyclic dienes lie on the same line.[1b] These data, together with the corresponding values for CHT and NA,[1c] are shown in Figure 2. We simply wish to point out here that the point for the CHT transient is at least in accord with its identification as ^{3}CHT*;[10] this was confirmed as follows.

3.2. Triplet Energy Transfer from CHT to Monitors. Pulse radiolysis of a deaerated toluene solution of CHT ($\sim 10^{-1}$ mol L^{-1}) containing the monitor perylene (Pe; $2–8 \times 10^{-4}$ mol L^{-1}) resulted in "slow" exponential grow-in of the monitor triplet according to eq 5 (Figure 3). A plot of the first-order constant for

$$^3\text{CHT}^* + \text{M} \xrightarrow{k_{et}} \text{CHT} + {}^3\text{M}^* \quad (5)$$

grow-in, k', against the monitor concentration (Figure 3) according to eq 6 gave a triplet energy transfer rate constant, k_{et}, of $6.6 \times$

$$k' = k_d + k_{et}[\text{M}] \quad (6)$$

10^9 L mol^{-1} s^{-1} and an intercept, $k_d = 1.9 \times 10^5$ s^{-1}, in good agreement with the rate constant for decay of the transient observed on pulse radiolysis of CHT alone in toluene, 1.4×10^5 s^{-1}. The Pe concentrations necessary to obtain accurate data of the type depicted in Figure 3 prevented the monitoring of the ^{3}CHT* decay corresponding to the ^{3}Pe* grow-in, a consequence of monitor ground-state absorption. This was possible however at a much lower Pe concentration of 4.0×10^{-5} mol L^{-1} when the rate of decay of ^{3}CHT* was still more than doubled. This decay at 320 nm and the corresponding grow-in of ^{3}Pe* at 490 nm yielded fortuitously identical k' values of 5.1×10^5 s^{-1}, reasonably close to the anticipated value of 4.6×10^5 s^{-1} based on the intercept and slope in Figure 3.

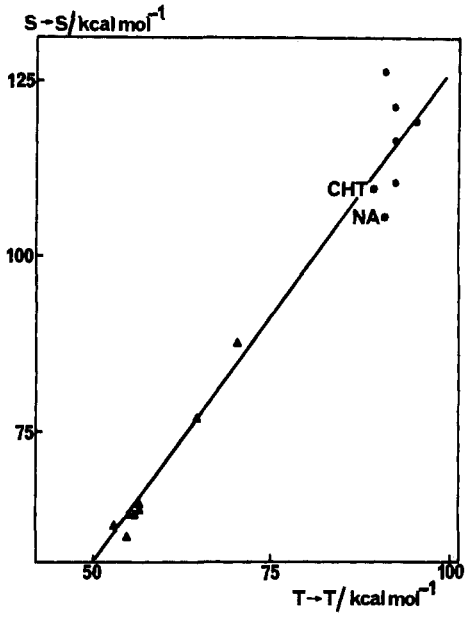


Figure 2. Singlet–singlet absorption maxima plotted against corresponding triplet–triplet absorption values for CHT and NA (*), 1,3-dienes (●),[1b] and retinal and related polyenes (▲).[9]

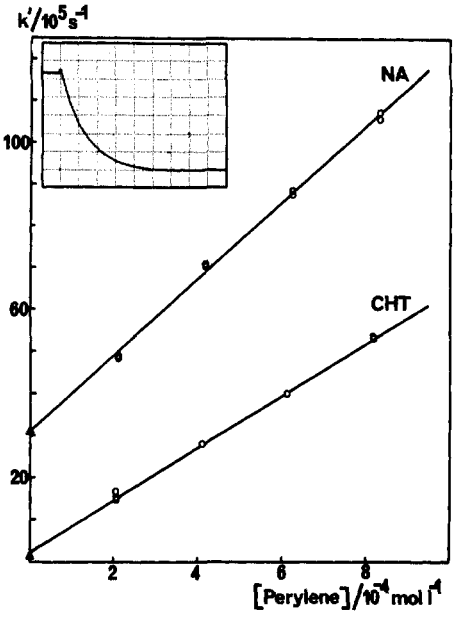


Figure 3. First-order constant for perylene triplet formation against perylene concentration for triplet energy transfer in toluene from CHT (7.7×10^{-2} mol L^{-1}) and NA (2.4×10^{-2} mol L^{-1}); the experimental points at zero concentration (▲) correspond to k_d for ^{3}CHT* and ^{3}NA* determined from triplet–triplet absorption measurements. The data for NA have been published[1c] and are shown here for comparative purposes. Inset: Time dependence of perylene triplet formation monitored at 490 nm after absorption of a 20-ns electron pulse by liquid toluene containing CHT (7.7×10^{-2} mol L^{-1}) and perylene (2.0×10^{-4} mol L^{-1}); 4.3% absorption/division, 500 ns/division.

(5) Berry, P. J.; Burton, M. *J. Chem. Phys.* **1955**, *23*, 1969.
(6) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.
(7) (a) Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 446. (b) Görner, H.; Schulte-Frohlinde, D. *Ibid.* **1981**, *85*, 1835. (c) Görner, H. *Ibid.* **1982**, *86*, 2028.
(8) Saltiel, J.; Thomas, B. *Chem. Phys. Lett.* **1976**, *37*, 147.
(9) Truscott, T. G.; Land, E. J.; Sykes, A. *Photochem. Photobiol.* **1973**, *17*, 43.
(10) We have already pointed out[1b] that such correlations must, in part, be fortuitous when one considers the variety of torsional geometries associated with both the ground states and relaxed triplets of both acyclic and cyclic dienes[1b] and now trienes.

Table I. Rate Constants (L mol^{-1} s^{-1})[a] for Triplet Energy Transfer in Toluene from CHT, NA, and Az to Monitors (M)

monitor (λ, nm)	E_T, kcal mol^{-1}	CHT → M	NA → M	Az → M
perylene (490)	35.1[b]	6.6×10^9	9.1×10^9[d]	9.4×10^9[e]
β-carotene (525)	<23.0[c]	1.1×10^{10}	1.2×10^{10}	1.2×10^{10}

[a] This work unless otherwise stated. [b] Reference 14. [c] Reference 15. [d] Reference 1c. [e] Reference 12.

Table II. Rate Constants (L mol^{-1} s^{-1})[a] for triplet Energy Transfer in Toluene from Monitors (M) to Cycloheptatriene (CHT) Neo-alloocimene (NA)

monitor (λ, nm)	E_T	M → CHT	M → NA
fluorene (370)	68.0[b]	6.8×10^9	6.3×10^9
biphenyl (370)	65.7[b]	5.9×10^9	7.4×10^9
naphthalene (420)	60.9[b]	5.2×10^9	6.5×10^9
chrysene (570)	56.6[b]	2.7×10^9	7.2×10^9
fluoranthene (415)	54.2[b]	8.1×10^8	3.2×10^9
pyrene (415)	48.2[c]	$1.9\ (1.7)^e \times 10^8$	4.1×10^9
acridine (440)	45.0[b]	3.2×10^7[e]	4.0×10^8[e]
anthracene (425)	42.7[d]	7.9×10^6[e]	5.3×10^7[e]

[a] Determined by pulse radiolysis unless otherwise stated. Monitoring wavelengths are indicated in column 1. [b] Reference 14, hydrocarbon glass at 77 K. [c] Reference 16, EPA glass at 77 K. [d] Reference 17, EPA glass at 77 K. [e] Determined by pulsed laser excitation.

These data confirm that we are dealing with the triene triplet state. In addition, we have confirmed that the ^{3}CHT* yield is that to be expected as a result of the efficient quenching of the toluene triplet states (^{3}T*) produced during the electron pulse. This has been achieved by comparison with azulene (Az) which was chosen because its singlet state does not intersystem cross.[11,2b] Thus, a comparison of ^{3}Az* and ^{3}CHT* yields reflects their production via ^{3}T* only. We have recently characterized ^{3}Az* in terms of lifetime and triplet energy in benzene by using the pulse radiolysis technique,[2b] and this work has been repeated with toluene as the solvent.[12] The values of immediate importance to the present work are for the rate constants in toluene for natural decay, $k_d = 9.3 \times 10^4$ s^{-1}, and for triplet energy transfer to Pe, $k_{et} = 9.4 \times 10^9$ L mol^{-1} s^{-1}, the corresponding values from the present work for CHT being 1.7×10^5 s^{-1}[13] and 6.6×10^9 L mol^{-1} s^{-1}, respectively. Thus, in the presence of added Pe (10^{-4} mol L^{-1}), the percentages of ^{3}Az* and ^{3}CHT* scavenged should be 91% and 80%, respectively; i.e., the yield of ^{3}Pe* from ^{3}CHT* should be 88% of that from an identical amount of ^{3}Az*. In light of these considerations, identical solutions of CHT and Az (10^{-2} mol L^{-1}) in toluene, each containing Pe (10^{-4} mol L^{-1}), were subjected to pulse radiolysis under identical conditions of radiation dose, etc. In each case the amount of ^{3}Pe* produced was determined by monitoring its grow-in to maximum absorption at 490 nm (cf. Figure 3). The maximum optical densities were 0.165 and 0.179 for the CHT and Az experiments, respectively. Thus, the yield from ^{3}CHT* was 92% of that from ^{3}Az*, in good agreement with the predicted value of 88%. This analysis of course depends on the reasonable assumption that energy transfer from ^{3}T* to both CHT and Az proceeds with approximately the same efficiency.

In Table I are shown the rate constants for triplet energy transfer from the triplet states of CHT, NA, and Az to both Pe and β-carotene. These values were determined as part of this work or as referenced. The conclusion from these data is that the "available" triplet energy of the relaxed ^{3}CHT* is below those of ^{3}NA* (~40 kcal mol^{-1})[1c,d] and ^{3}Az* (39.8 kcal mol^{-1})[12] but above that of Pe (35.1 kcal mol^{-1}).[14] This has been confirmed by establishment of a triplet energy transfer equilibrium between CHT and anthracene as described in section 3.5.

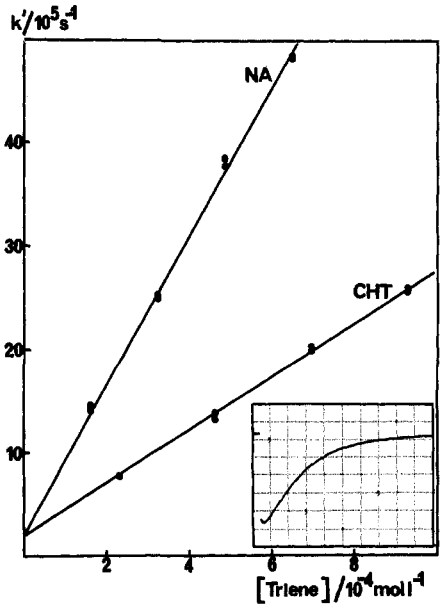


Figure 4. First-order constant for chrysene triplet decay in toluene against CHT and NA concentrations. Inset: Time dependence of chrysene triplet decay monitored at 570 nm after absorption of a 20-ns electron pulse by liquid toluene containing chrysene (9.4×10^{-3} mol L^{-1}) and CHT (9.3×10^{-4} mol L^{-1}); 11.1% absorption/division, 200 ns/division.

3.3. Triplet Energy Transfer from Monitors to CHT and NA. Pulse radiolysis of deaerated solutions of monitors (~10^{-2} mol L^{-1}) containing varying concentrations of CHT or NA (<10^{-3} mol L^{-1}) allowed routine determination of the rate constants for energy transfer from ^{3}M* (eq 7) for the monitors fluorene to pyrene in Table II. Plots of the first-order constant for ^{3}M* decay, k', vs.

$$^3\text{M}^* + \text{CHT or NA} \xrightarrow{k_{et}} \text{M} + {}^3\text{CHT}^* \text{or } {}^3\text{NA}^* \quad (7)$$

[CHT or NA] according to eq 8 gave the triplet energy transfer

$$k' = k_{dM} + k_{et}[\text{CHT or NA}] \quad (8)$$

rate constant, k_{et}, and an intercept corresponding to the natural decay of ^{3}M* under the experimental conditions, k_{dM}. Typical data for chrysene are reproduced in Figure 4.

In situations where it is necessary to examine the decay of a monitor triplet state in the presence of high concentrations of a poor quencher, the direct excitation of quencher by the toluene triplet states becomes a problem in pulse radiolysis experiments, particularly if reverse transfer of triplet energy is possible. For such situations, laser excitation of low monitor concentrations is a much more satisfactory technique since back transfer may be minimized. Thus, for the quenching by NA and CHT of the lowest energy monitor triplets of Table II, i.e., those of acridine and anthracene, pulsed laser excitation at 355 nm of low concentrations, 6×10^{-5} and 9×10^{-5} mol L^{-1}, respectively, was employed.[18]

It has been rightly pointed out by the reviewers that the significance (vide infra) of the rate constants listed in Table II would be enhanced if it could be demonstrated that they do indeed correspond to triplet energy transfer processes, particularly of course where they are orders of magnitude down on diffusion control. The lowest energy triplet monitor listed is anthracene (An) and we have been able to show that the quenchings of ^{3}An* by NA[1c,d] and by CHT (section 3.5) do indeed involve triplet

(11) Görner, H.; Schulte-Frohlinde, D. *J. Photochem.* **1981**, *16*, 169.
(12) Gorman, A. A.; Hamblett, I.; Harrison, R. J., unpublished data.
(13) This is the mean of values determined from triplet–triplet absorption (1.4×10^5 L mol^{-1} s^{-1}) and triplet energy transfer (1.9×10^5 L mol^{-1} s^{-1}) experiments.
(14) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.
(15) Farmilo, A.; Wilkinson, F. *Photochem. Photobiol.* **1973**, *18*, 447. Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.
(16) Clar, E.; Zander, M. *Chem. Ber.* **1956**, *89*, 749.
(17) Padhye, M. R.; McGlynn, S. P.; Kasha, M. *J. Chem. Phys.* **1956**, *24*, 588.
(18) As an additional check, it was shown that essentially identical rate constants for the quenching of pyrene triplet by CHT were obtained by pulse radiolysis and laser photolysis (cf. Table II).

Table III. Concentrations (mol L^{-1})[a] for Pulse Radiolysis Experiments in Toluene

expt	reactants	[^{3}CHT*]	[^{3}An*]	[^{3}Pe*]
A	CHT (2.0×10^{-1})	1.3×10^{-5} (imm.)[b]	2.5×10^{-6} (imm.)[e,f]	
[establishment of equilib]	An (2.0×10^{-2})	$(1.3 \pm 0.3) \times 10^{-5}$ (eq.)[c]	8.4×10^{-7} (eq.)[f]	
B	CHT (2.2×10^{-1})	1.4×10^{-5} (imm.)[d]		1.4×10^{-5} (max.)
[actinometry]	Pe (5.0×10^{-4})			

[a] Concentrations (two significant figures only) are denoted as "immediate" (imm.), at equilibrium, arrowed time in Figure 6 (eq.), or maximum (max.). [b] Calculated from corresponding value from experiment B. [c] Reference 23. [d] Calculated from rate constants given in section 3.2 and the maximum [^{3}Pe*]. [e] Reference 24. [f] Reference 25.

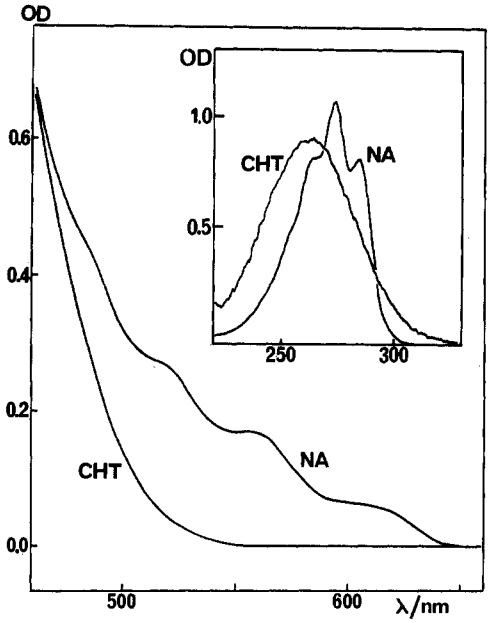


Figure 5. Absorption spectra of CHT/CH_2I_2 (1:1, v/v) and NA/CH_2I_2 (1:1, v/v); path lengths 5 cm, reference toluene/CH_2I_2 (1:1, v/v). Inset: absorption spectra of CHT (3.6×10^{-4} mol L^{-1}) and NA (1.5×10^{-5} mol L^{-1}) in cyclohexane; path lengths 1 cm.

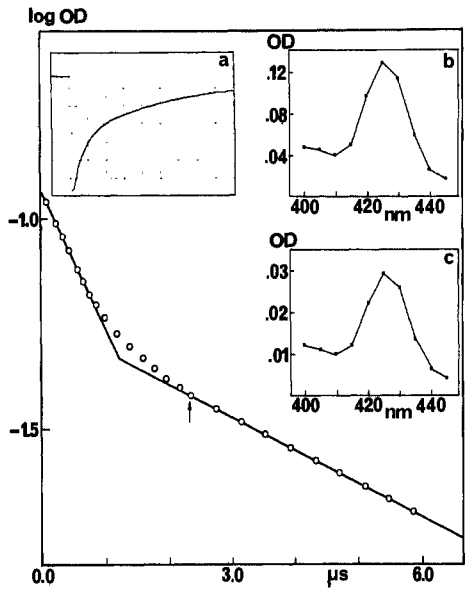


Figure 6. Semilogarithmic plot for transient absorption monitored at 425 nm after absorption of a 20-ns electron pulse by deaerated toluene containing CHT (2.0×10^{-1} mol L^{-1}) and An (2.0×10^{-2} mol L^{-1}). Insets: (a) Corresponding time dependence of transient absorption monitored at 425 nm, 3.5% absorption/division, 1 μs/division; (b and c) corresponding transient absorption spectra measured 200 ns and 5 μs, respectively, after the electron pulse.

energy transfer. It is therefore reasonable to assume that the same is true for the higher triplet energy monitors listed in Table II.

3.4. Electronic Absorption Spectra of CHT and NA. In Figure 5 are shown the electronic absorption spectra above 450 nm of CHT and NA measured under heavy atom perturbation conditions of the type previously described.[19] That of NA shows a progression of bands, very similar to those previously observed for related acyclic trienes,[19] and the longest wavelength band at 607 nm corresponds to a singlet–triplet transition energy of 47.1 kcal mol^{-1}. In the case of CHT, no such banded spectrum is observed, the onset of absorption at 550 nm being followed by a smooth increase in optical density. This behavior reflects the character of the singlet–singlet spectra of the two trienes in hydrocarbon solvents (Figure 5, inset), NA exhibiting typical banded polyene structure, CHT an unusually smooth absorption curve. Clearly the higher energies associated with the CHT transitions reflect the lower degree of conjugation in its boatlike ground state.[20] The difference between the *onsets* of the singlet–triplet absorption of CHT (550 nm) and NA (650 nm) corresponds to a ΔE_T value of 7.9 kcal mol^{-1}. Arbitrarily approximating this difference to the 0,0 transitions puts that of CHT at ~55 kcal mol^{-1}. Since optimum rate constants for exothermic triplet energy transfer between organic molecules in benzene and toluene are normally in the $5-10 \times 10^9$ L mol^{-1} s^{-1} range and in the isoenergetic region fall by a factor of ~2, a consideration of Table II would place the spectroscopic triplet energies of NA and CHT at just less than that of pyrene (48.2 kcal mol^{-1}) and approximately equal to that of chrysene (56.6 kcal mol^{-1}), respectively. These values are in reasonable agreement with those of 47.1 and ~55 kcal mol^{-1} extracted from Figure 5. While conceding the approximate nature of the above approach, it is clear that the spectroscopic triplet energy of CHT is of the order of 55–56 kcal mol^{-1}.

3.5. Triplet Energy Transfer Equilibration between Anthracene and CHT. When the energy difference between a triplet donor and acceptor decreases to ~4 kcal mol^{-1}, back-transfer of triplet energy may become important.[21] If appropriate concentrations of donor and acceptor can be achieved, it is possible to observe the time-resolved establishment of an equilibrium between the two triplet states if their natural decays are slow relative to the energy-transfer processes. Work of this type has been described previously.[1a,2,22] We have recently been able to demonstrate the reversibility of triplet energy transfer between anthracene (An) and NA[1c,d] as a consequence of the fact that the spectroscopic (47.1 kcal mol^{-1}) and relaxed (~40 kcal mol^{-1}) triplet energies of NA are both reasonably close to that of An (42.7 kcal mol^{-1}),[17] thus making triplet energy transfer a significant process in both directions. It was not possible however to demonstrate the establishment of a true equilibrium. In this section, we demonstrate the establishment of such an equilibrium for triplet energy transfer between An and CHT (eq 9) which is all the more remarkable

$$^3\text{An}^* + \text{CHT} \underset{k_{et}^b}{\overset{k_{et}^f}{\rightleftharpoons}} \text{An} + {}^3\text{CHT}^* \qquad (9)$$

because the difference in triplet energies between the spectroscopic

(19) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.
(20) (a) Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 458. (b) Jensen, F. R.; Smith, L. A. *Ibid.* **1964**, *86*, 956. (c) Traetteberg, M. *Ibid.* **1964**, *86*, 4265.
(21) (a) Sandros, K.; Bäckström, H. L. J. *Acta. Chem. Scand.* **1962**, *16*, 958. (b) Sandros, K. *Ibid.* **1964**, *18*, 2355.
(22) Kikuchi, K.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2732. Kira, A.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 196.

and relaxed forms of ^{3}CHT* turns out to be 17–18 kcal mol^{-1}, ~10 kcal mol^{-1} larger than the corresponding value for the acyclic ^{3}NA*.[1c,d] Two experiments have been performed. Experiment A has allowed establishment of the equilibrium; experiment B has served as an actinometer to determine the triplet-state concentrations associated with the equilibrium. The results are summarized in Table III.

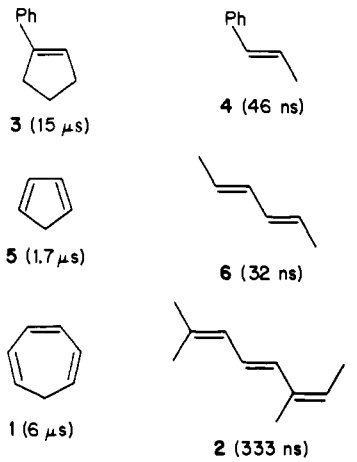
(A) Establishment of the Equilibrium. Pulse radiolysis of a deaerated toluene solution of CHT (2.0×10^{-1} mol L^{-1}) and An (2.0×10^{-2} mol L^{-1}) resulted in "immediate" formation of ^{3}An* followed by exponential decay to an equilibrium position and subsequent bleeding of this equilibrium (Figure 6). This interpretation was confirmed by the fact that the spectrum of the absorbing species was identical with that of ^{3}An* for both the fast and slow components of the decay as shown in Figure 6. In this figure is also shown a semilogarithmic plot of log OD vs. time for the ^{3}An* decay monitored at 425 nm. In order to determine the equilibrium constant, it was necessary to establish the ^{3}CHT* and ^{3}An* concentrations at or after the arrowed time in Figure 6. This has been carried out as follows.

(B) Actinometry. Pulse radiolysis of a deaerated toluene solution of CHT (2.2×10^{-1} mol L^{-1}) and Pe (5×10^{-4} mol L^{-1}) under conditions of radiation dose, etc., which were identical with those of the experiment depicted in Figure 6 allowed determination of the initial ^{3}CHT* concentration as 1.4×10^{-5} mol L^{-1} (cf. section 3.2). Thus, in the experiment shown in Figure 6 (cf. Table III, experiment A), the initial ^{3}CHT* and ^{3}An* concentrations as a result of scavenging ^{3}T* (eq 1) should be 1.3×10^{-5} (ten-elevenths) and 1.3×10^{-6} (one-eleventh) mol L^{-1}, respectively, assuming that the rate constants for highly exothermic triplet energy transfer from ^{3}T* to CHT and An are essentially the same.[24] This allows the concentration of ^{3}CHT* at the arrowed time in Figure 6 to be placed at $1.3 \pm 0.3 \times 10^{-5}$ mol L^{-1}.[23] The corresponding ^{3}An* concentration of 8.4×10^{-7} mol L^{-1} was determined from its optical density and known extinction coefficient.[25] Assuming an error of ±25% in k_{et}^f/k_{et}^b determinations[1a,2] of this kind, a value of 1.6 ± 0.8 results from the data in Table III. The experimental value for k_{et}^f of 7.9×10^6 L mol^{-1} s^{-1} (Table II, eq 9) thus leads to a rate constant of $(6.1 \pm 2.8) \times 10^6$ L mol^{-1} s^{-1} for triplet energy transfer from CHT to An, k_{et}^b. Assuming that this corresponds to vertical transfer which obeys the Sandros equation,[21b] eq 10, where k_D, the rate constant for diffusion, is

$$k_{et} = k_D e^{-\Delta E_T/RT} \quad (10)$$

taken as 1.5×10^{10} L mol^{-1} s^{-1},[1d] the energy gap, ΔE_T, between the relaxed ^{3}CHT* and ^{3}An* is 4.7 ± 0.3 kcal mol^{-1}. This places the relaxed ^{3}CHT* at ~38 kcal mol^{-1}, 17–18 kcal mol^{-1} below that of the spectroscopic state (55–56 kcal mol^{-1}; cf. section 3.4). This relaxed value of ~38 kcal mol^{-1} is in excellent agreement with the earlier conclusions (section 3.2) that it lies between those of Pe (35.1 kcal mol^{-1}) and Az (39.8 kcal mol^{-1}).[27]

Chart I



The ratio [^{3}CHT*]/[^{3}An*] at equilibrium, 16.5 ± 7.6, leads to the prediction that the equilibrium should be bled with a rate constant essentially identical with the natural decay constant of ^{3}CHT* even though ^{3}An* has a much longer lifetime. The experimental value (Figure 6) is 1.7×10^5 s^{-1}, identical with the mean of the values determined in sections 3.1 and 3.2. We therefore place the ^{3}CHT* lifetime at 6 ± 1 μs. The fact that the equilibrium decays with this lifetime is excellent evidence that the quenching of ^{3}An* by CHT involves nothing significant other than triplet energy transfer. All the quenching rate constants listed in Table II can therefore be safely assumed to reflect triplet energy transfer only.

4. Discussion

The data described in section 3 provide a satisfactory characterization of the triplet state of CHT. Two results of particular interest arising from these data are (a) that although the lifetime of ^{3}CHT* (6 ± 1 μs) is considerably longer than that of ^{3}NA* (333 ns), its relaxed triplet energy is *less*, despite the reverse being the case for the corresponding spectroscopic states, and (b) that in the endothermic situation, CHT is clearly a "nonvertical" acceptor of triplet energy. These characteristics will be discussed in that order.

4.1. Comparison of Triplet Lifetimes and Relaxed Triplet Energies. The properties of olefin triplet states are clearly critically dependent on the relationship between the S_0 and T_1 potential energy surfaces and in particular the vertical distance between the minimum on the T_1 surface and S_0. Where other minima of similar energy are accessible under the prevailing conditions, the stilbenes being a case in point,[7b,28] the situation becomes more complex. What is certain is that deactivation to S_0 is nonradiative and involves spin-forbidden intersystem crossing. Franck–Condon restrictions on this process become less the smaller the $T_1 - S_0$ gap, and in addition certain structural features within T_1 may accelerate the process as a result of favorable spin–orbit coupling factors. While the theory of nonradiative transitions in flexible olefins is not fully developed, work on the stilbenes[29] and styrenes[30] has increased understanding of the principal factors governing intersystem crossing within such molecules. Deuterium labeling studies indicate that, as for planar aromatic hydrocarbons, the funneling of energy into the vibrational modes of C–H bonds is of particular importance. In addition, it appears established experimentally that C–H bonds attached to carbon involved in

(23) For the sake of simplicity, we have placed obvious limits on the ^{3}CHT* concentration at the arrowed time in Figure 6. These are (a) that expected on the basis of natural exponential decay ($k_d = 1.7 \times 10^5$ s^{-1})[13] from the initial concentration of 1.4×10^{-5} mol L^{-1} with insignificant energy transfer from ^{3}An* (lower limit = 1.0×10^{-5} mol L^{-1}) and (b) that expected for no significant natural decay and assuming ^{3}An* lost equals ^{3}CHT* gained (upper limit = 1.5×10^{-5} mol L^{-1}). These lead to the quoted value of $(1.3 \pm 0.3) \times 10^{-5}$ mol L^{-1}.

(24) We have shown that for pulse radiolysis of toluene solutions of CHT (10^{-1} mol L^{-1}) and An (10^{-3} mol L^{-1}) where An cannot compete effectively for ^{3}T*, some "immediate" ^{3}An* absorption is still observed. This is due to the fact that CHT does not compete as effectively for ^{1}T* as for instance does NA[1c,d] (cf. $S_0 \rightarrow S_1$ absorption in Figure 5, inset). Hence, some ^{1}An* is formed and intersystem crosses to give "immediate" ^{3}An*. Thus, in experiment A (Table III), it was anticipated that the "immediate" concentration of ^{3}An* would be larger than that expected from the quenching of ^{3}T* (1.3×10^{-6} mol L^{-1}). This was the case.

(25) To determine ^{3}An* and ^{3}Pe* concentrations, we have employed the triplet–triplet extinction coefficients of Bensasson and Land.[26] Although values for benzene were used, this is a valid exercise since the triplet–triplet absorption spectra of these monitors in toluene are virtually indistinguishable from those in benzene. It should be emphasized that the accuracy of the current work depends only on the much more certain *relative* values of these extinction coefficients rather than on their absolute magnitudes.

(26) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163.

(27) If the Sandros equation is not obeyed, i.e., $k_{et}^b > k_D e^{-\Delta E_T/RT}$, the triplet energy of ^{3}CHT* would be *less* than ~38 kcal mol^{-1}. The difference cannot be great since triplet energy transfer to Pe (35.1 kcal mol^{-1}) is fast (6.6×10^9 L mol^{-1} s^{-1}).

(28) Saltiel, J.; Rousseau, A. D.; Thomas, B. *J. Am. Chem. Soc.* **1983**, *105*, 7631 and references therein.

(29) Saltiel, J.; D'Agostino, J.; Herkstroeter, W. G.; Saint-Ruf, G.; Buce-Hoi, N. P. *J. Am. Chem. Soc.* **1973**, *95*, 2543.

(30) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

torsional relaxation from planar geometries are the most important in this respect and therefore substitution of such hydrogens by other groups increases triplet lifetimes.[7c,30,31] It has also been argued on theoretical grounds that the greater the degree of orthogonality and the smaller the average separation between the uncoupled electrons, the more efficient will be the spin inversion process.[32] Experimental support of such proposals is largely lacking (cf. ref 33). In light of the above facts, we have compared the triplet lifetimes and triplet energies of CHT and NA both with each other[34] and with relevant monoolefin (**3** and **4**) and diene (**5** and **6**) pairs. Structures and triplet lifetimes are reproduced in Chart I.

Theoretical calculations indicate clearly that, on spectroscopic excitation, the simpler the olefinic system in terms of conjugation, the *more* favorable will be torsion within T_1 and the *less* favored will be the same torsion within S_0. The classic consequence of this fact is that for isolated double bonds in acyclic systems, S_0 and T_1 cross or nearly cross at an angle of twist of 90°.[36] The net result is fast intersystem crossing and vibrational relaxation to planar S_0. Although failure to observe triplet energy transfer from such systems has naturally been attributed to the resulting extremely short lifetimes,[37] it is clear that if S_0 and T_1 are effectively isoenergetic, there will be no electronic energy to transfer. The systems most closely related to the simple olefins, and for which lifetime data exist, are the styrenes and phenylcycloalkenes examined by Caldwell and Cao.[30] These are typified by 1-phenylcyclopentene (**3**) and (*E*)-1-phenylpropene (**4**) which exhibit triplet lifetimes of 15 ± 1 μs and 46 ns, respectively. The authors argued persuasively that the acyclic triplets are fully twisted and that the much longer triplet lifetime of the cyclopentene reflects (a) a significant energy difference between S_0 and the relaxed T_1 which certainly cannot achieve the perpendicular configuration and (b) a consequent decrease in spin–orbit coupling. To our knowledge, there is no published data concerning the relaxed triplet energies of molecules of the above types.

The triplet lifetimes of cyclopentadiene (**5**; 1.7 μs)[1a] and (*E*,-*E*)-2,4-hexadiene (**6**; 32 ns)[31] follow a similar pattern, indicating a significant degree of relaxation in the case of **6** and a smaller $T_1 - S_0$ gap than for **5**. This is confirmed by a knowledge of the spectroscopic and relaxed triplet energies of cyclopentadiene (58.3[38] and 58.0[1a] kcal mol^{-1}, respectively) and 2,5-dimethyl-2,4-hexadiene (59–60[38] and ~42[1a] kcal mol^{-1}, respectively), a reasonable model for **6**. In the cases of both 1-phenylcycloalkenes and cyclic 1,3-dienes, ring enlargement allows greater torsional relaxation to the extent that for ring sizes of seven (alkenes)[30] and eight (dienes),[1b] triplet lifetimes are as for the corresponding acyclic systems.

The lifetimes of CHT (**1**; 6 μs) and NA (**2**; 333 ns) clearly show the same trend as the **3**/**4** and **5**/**6** pairs (Chart I), and at first sight one might be tempted to attribute the same explanation, relaxation in ^{3}NA*, lack of relaxation in ^{3}CHT*. However, for reasons outlined below, this cannot be the case.

Firstly, it should be said that the triplet lifetime of NA (333 ns) is fairly typical in that the corresponding value for (*E*)-1,3,5-hexatriene is 300 ns.[39] The relatively small influence of

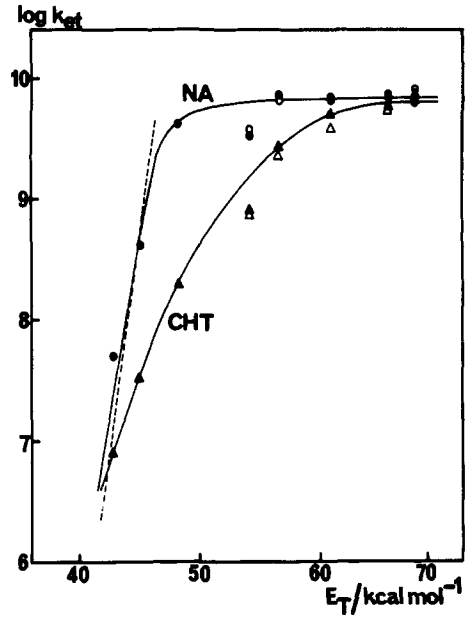


Figure 7. Plots of log k_{et} vs. monitor triplet energy for quenching of monitor triplets by CHT (▲) and NA (●). Additional data points are for *cis*-stilbene (△) and *trans*-stilbene (○). See Table II for monitor identity and section 4.2 for the significance of the dashed line.

the four methyl groups could be a consequence, at least in part, of relaxation which predominantly involves torsion about the central bond of the π system which has the same substitution pattern in both NA and (*E*)-1,3,5-hexatriene. In the case of CHT, the lack of substituents and the relaxed triplet energy (~38 kcal mol^{-1}) which is lower than that of NA should facilitate spin inversion. The extremely long 6-μs lifetime of ^{3}CHT* cannot therefore be explained on the basis of either substituent effects or the energy gap law. We are therefore forced to the conclusion that the controlling factor is a geometry which inhibits the spin-inversion process, the obvious candidate being one which is essentially planar. In its ground state, CHT possesses a rigid boatlike structure in which the torsional angles between the formal terminal and central double bonds of the π system are ~40°.[20c] In the first excited state of a 1,3,5-hexatriene, the C(2)–C(3) and C(4)–C(5) bond orders are increased at the expense of those between C(1)–C(2), C(3)–C(4), and C(5)–C(6).[40] It is not unreasonable that this effect and the greater flexibility within an electronically excited state as opposed to a ground state should lead to a close to planar geometry.

We initially considered that the large loss of "available" triplet energy on relaxation of ^{3}CHT* (17–18 kcal mol^{-1}) compared with that for ^{3}NA* (~7 kcal mol^{-1})[1c,d] simply reflected the greater degree of π-electron localization in CHT due to its nonplanar ground-state structure. In other words, twisting about a formal, more alkene-like double bond would result in particularly steep changes in the S_0 and T_1 potential energy surfaces, thus bringing them closer together at the T_1 equilibrium geometry than in the case of NA, even though the spectroscopic energy gap for the latter is much less. Although such a relatively rapid surface approach must occur for CHT, the torsion involved must, if our proposal is correct, take place about the formal single bonds of the π system. Although this is in contrast to the anticipated torsion of planar trienes,[41] it makes sense. Thus, planar triene triplets resist torsion about the C(2)–C(3) and C(4)–C(5) bonds because of the increased π-bond order, ^{3}CHT*, which, when initially produced, is twisted about those bonds, undergoes C(2)–C(3) and C(4)–C(5) torsion to remove this twist because of the increased π-bond order.[42]

(31) Caldwell, R. A.; Singh, M. *J. Am. Chem. Soc.* **1982**, *104*, 6121.
(32) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18. Shaik, S. S. *Ibid.* **1979**, *101*, 2736.
(33) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *9*, 1167.
(34) This comparison is valid in the sense that the lifetimes of ^{3}NA* and ^{3}CHT* are not shortened by σ-bond forming chemical processes; NA appears to undergo geometric isomerization essentially exclusively,[35] and, in our hands, CHT was chemically inert to triplet sensitization.
(35) Butt, Y. C. C.; Singh, A. K.; Baretz, B. H.; Liu, R. S. H. *J. Phys. Chem.* **1981**, *85*, 2091 and references therein.
(36) Mercer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639. Mulliken, R. S. *J. Chem. Phys.* **1977**, *66*, 2448. Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89. Kollmar, H.; Staemmler, V. *Ibid.* **1978**, *48*, 223. Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. III.
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(38) Evans, D. F. *J. Chem. Soc.* **1960**, 1735.
(39) Gorman, A. A.; Hamblett, I.; Sykes, L., unpublished data.
(40) Simmons, H. E. *Prog. Phys. Org. Chem.* **1970**, *7*, 1.
(41) Hoffmann, R. *Tetrahedron* **1966**, *22*, 521. Baird, N. C.; West, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 4427. Bonačić-Koutecký, V.; Shingo-Ishimaru, *Ibid.* **1977**, *99*, 8134. Ohmine, I.; Morokuma, K. *J. Chem. Phys.* **1980**, *73*, 1907.

Table IV. Rate Constants (L mol^{-1} s^{-1})[a] for Triplet Energy Transfer in Toluene from Monitors (M) to *trans*- and *cis*-Stilbene

monitor (λ, nm)	E_T[b]	M → *trans*-stilbene	M → *cis*-stilbene
fluorene (370)	68.0	8.1×10^9	6.4×10^9
biphenyl (370)	65.7	7.7×10^9	5.7×10^9
naphthalene (420)	60.9	6.9×10^9	3.8×10^9
chrysene (570)	56.6	6.3×10^9	2.3×10^9
fluoranthene (415)	54.2	3.8×10^9	7.4×10^8

[a] Determined by pulse radiolysis. [b] Reference 14.

4.2. "Nonvertical" Triplet Energy Transfer to CHT. Rate constants for vertical endothermic triplet energy transfer are generally thought to conform to eq 10 where ΔE_T is the energy difference between the 0,0 Franck–Condon-allowed $S_0 \rightarrow T_1$ transitions of donor and acceptor and k_D is the rate constant for diffusion.[21b] Deviations from this equation were first noted for *cis*-stilbene as the energy acceptor.[43] For this molecule, endothermic triplet energy transfer is faster than predicted by eq 10, and such behavior is said to be characteristic of energy acceptors which have significantly different equilibrium geometries in their ground and lowest triplet states. In Figure 7 are shown log k_{et} vs. donor triplet energy plots for the quenching of the triplets of the monitors listed in Table II by CHT and NA, together with the theoretical line predicted by eq 10 for an acceptor requiring 47.1 kcal mol^{-1} of electronic excitation energy (the spectroscopic value for NA) and a value for k_D of 1.5×10^{10} L mol^{-1} s^{-1}. The immediate conclusion from these plots is that whereas NA exhibits something close to vertical behavior, CHT is quite clearly a "nonvertical" acceptor of triplet energy, whatever that phraseology might mean, in the endothermic situation. It so happens that the spectroscopic triplet energies of *cis*-stilbene (~59 kcal mol^{-1})[44] and *trans*-stilbene (~49 kcal mol^{-1})[44] are not very different from those of CHT (~56 kcal mol^{-1}) and NA (47.1 kcal mol^{-1}), respectively. In Figure 7, we have included data points for the quenching of the five monitor triplets of highest energies by *cis*- and *trans*-stilbene (Table IV). The rate constants were determined by pulse radiolysis in the usual way, and the similarity in the behavior of the CHT/*cis*-stilbene and NA/*trans*-stilbene pairs is readily apparent from Figure 7.[45]

There has been considerable discussion concerning the origins of the nonvertical transfer phenomenon, and, of course, the behavior of *cis*-stilbene has been central to such discussion.[44e] In their original proposals, Hammond and Saltiel suggested relaxation of Franck–Condon requirements owing to (a) a longer interaction time of the donor/acceptor pair relative to a photon absorption process and/or (b) interaction between donor and acceptor electronic systems with resulting coupling of vibrational motions in the two molecules.[43a] It has been proposed that such coupling may take place within a complex or exciplex which is long-lived relative to the encounter complex.[46] Subsequently, Bylena[47] and then Yamauchi and Azumi[48] proposed that the requisite twisting is no greater than that to be inferred on the basis of $S_0 \rightarrow T_1$ absorption characteristics, proposals later questioned by Saltiel et al,[49] on the basis of variable-temperature experiments. It has also been concluded that the "hot band" mechanism,[50] i.e., thermal population of ground-state geometries corresponding to energetically favorable changes on the T_1 surface, is sufficient to explain observed phenomena.[51] A generalized classical treatment[52] and a quantum mechanical treatment applied to the stilbene problem[53] have led to the conclusion that behavior of the type exhibited by *cis*-stilbene can be accommodated on the basis of available spectroscopic data without involving the concept of "nonverticality". However, in contrast to this conclusion, a recent publication by Saltiel et al.[54] reports that for endothermic triplet energy transfer, both *trans*- and *cis*-stilbene are nonvertical acceptors. The key findings leading to this conclusion were that the extra energy requirement for both *trans*- and *cis*-stilbene to quench the triplet state of 9,10-dichloroanthracene (40.3 kcal mol^{-1}) relative to that of anthracene (42.7 kcal mol^{-1}) was reflected in a more negative entropy of activation as opposed to an increased enthalpy of activation. This result appears of critical importance. However, the observed rate constant, determined by flash photolysis, for the quenching of 9,10-dichloroanthracene triplet by, for instance, *trans*-stilbene was as low as 3×10^3 L mol^{-1} s^{-1} at room temperature, if anything a little less than the value to be anticipated for vertical excitation. It certainly needs to be proven that such extremely low rate constants actually correspond predominantly to triplet energy transfer processes.

4.3. Vibrational Level Density Contribution to "Nonvertical" Triplet Energy Transfer? We have shown that CHT is a "nonvertical" acceptor of triplet energy and mimics *cis*-stilbene in this respect. Behavior of this type is also exhibited by the (*E*)- and (*Z*)-1,2-diphenylpropenes.[43b] Whereas it has been proposed[55] that acyclic 1,3-dienes are also nonvertical acceptors of triplet energy, the currently available evidence[1a] indicates that this is not the case. Thus, to our knowledge, *established* "nonvertical" behavior in the case of olefins is restricted, not to those molecules with different S_0 and T_1 equilibrium geometries[52] but more specifically to those with nonplanar π systems in the ground state.[56] A comparison of the $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ spectra of CHT and NA (Figure 5), the $S_0 \rightarrow T_1$ spectra of *cis*-stilbene[44a,c,d] and *trans*-stilbene,[44a,b,d] and the $S_0 \rightarrow S_1$ spectra of the stilbenes and 1,2-diphenylpropenes[60] shows that whereas all spectra of NA and *trans*-stilbene show vibrational structure, those of the nonplanar, "nonvertical" acceptors are more or less structureless. This lack of structure in the $S_0 \rightarrow S_1$ spectra of the nonplanar stilbenes has of course already been commented upon within the photochemical context (cf. ref 44e). An obvious interpretation of these facts is that the nonplanar olefins have a greater density of populable vibrational levels in both S_1 and T_1 than do the essentially planar molecules.

The triplet energy transfer process can of course be considered as a nonradiative transition within a weak bimolecular complex.[61] In such an interpretation of a nonresonance energy transfer

(42) As a referee has pointed out, any deviation from planarity that may exist as a consequence of ring strain is likely to involve torsion about the formal double bonds of the π system for which the π-bond order has decreased. We can of course only agree with this comment.

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(45) In Figure 6, all four rate constants for the quenching of the fluoranthene triplet (54.2 kcal mol^{-1}) appear lower than anticipated. We have no explanation for this.

(46) Turro, N. J.; Dalton, J. C.; Weiss, D. S. *Org. Photochem.* **1971**, *2*, 1. Turro, N. J. "Modern Molecular Photochemistry"; W. A. Benjamin: Menlo Park, CA, 1978.

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(55) Liu, R. S. H.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 3406. Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *Ibid.* **1966**, *88*, 4781.

(56) Phenyl/olefin torsional angles have been reported for *trans*-stilbene (0 ± 7°; X-ray),[57] *cis*-stilbene derivatives (35–40°; X-ray),[58] (*E*)-1,2-diphenylpropene (34.5°; UV),[59] and (*Z*)-1,2-diphenylpropene (40°; UV).[59]

(57) Bernstein, J. *Acta. Crystallogr., Sect. B* **1975**, *31*, 1268. Hoekstra, A.; Meertens, P.; Vos, A. *Ibid.* **1975**, *31*, 2813.

(58) Durant, F.; Lefeure, F.; Norberg, B.; Evrard, G. *Cryst. Struct. Commun.* **1982**, *11*, 983.

(59) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 396.

(60) Jaffé, H. H.; Orchin, M. "Theory and Applications of Uitraviolet Spectroscopy"; Wiley: New York, 1962; Chapter 15.

(61) Robinson, G. W.; Frosch, R. P. J. *Chem. Phys.* **1962**, *37*, 1962; **1963**, *38*, 1187.

process, the rate constant for that transfer is given by eq 11 where

$$k_{et} = \frac{2\pi}{h}\beta^2 F\rho \qquad (11)$$

β is the electronic matrix element for the mixing of the initial and final states, F is the Franck–Condon factor for the transition, and ρ is the density of final states. The latter two parameters are clearly intimately related. The above considerations suggest the possibility that endothermic triplet energy transfer to the nonplanar π systems under consideration may, at least in part, be faster than predicted by the Sandros equation (eq 10) as a consequence of a high available T_1 vibrational level density relative to the planar systems which appear to conform with this equation. Structural features, including symmetry, which result in a high density of low-frequency vibrations in S_1 and T_1 may well lead to a similar situation in S_0, a situation which would also facilitate operation of the "hot band" mechanism.

We raise the above possibility more as a query than as a proposal. It is worth pointing out that if "nonvertical" behavior was essentially a vibrational state density phenomenon, there should be a whole range of degrees of "nonvertical" behavior, that of *cis*-stilbene, the 1,2-diphenylpropenes, and CHT being extreme enough to readily allow experimental detection.

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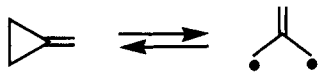
Upper Excited State(s) in the Methylenecyclopropane/Trimethylenemethane System. Photolysis of (*E*)- and (*Z*)-2,3-Diethyl-2-methylmethylenecyclopropane at 185 nm

Thomas Baum, Angelo Rossi, and R. Srinivasan*

Contribution from IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, and the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268. *Received October 15, 1984*

Abstract: From the photolysis of the title compounds in solution at 185 nm, it is possible to obtain all the possible methylenecyclopropane rearrangement products in about equal amounts. This contrasts with the thermal rearrangement which leads to mostly (>80%) one rearranged product. It is suggested that the photochemical rearrangement proceeds from a $\pi \rightarrow \pi^*$ excited state of methylenecyclopropane to the energy surface of a high-lying excited state of trimethylenemethane such as the $^1A'_1$ state (D_{3h} symmetry) but mixes with the lower ($^1A_1$) surface and leads to products. The other important photochemical process leads to an olefin and acetylene with retention of the stereochemistry.

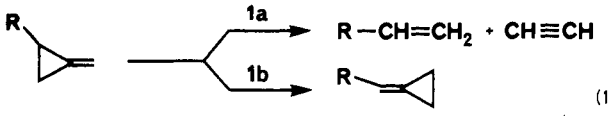
The intense theoretical interest that has been displayed in recent years in the ground and excited states of trimethylenemethane (TMM)[1] has resulted in numerous experimental investigations of the thermal transformation:[2]



methylene-cyclopropane TMM

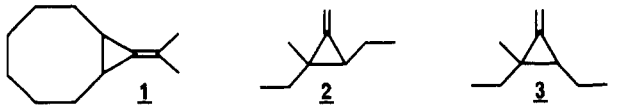
Although several studies on the photochemistry of methylenecyclopropane have been reported (see below),[3] they have provided very limited insight into the equilibrium given above.

Gas-phase photolysis at 147 and 124 nm of methylenecyclopropane itself resulted in total fragmentation of the molecule.[4] Many investigations have been carried out in solution with radiation of wavelength >200 nm on derivatives of methylenecyclopropane and especially those with conjugating phenyl groups.[5] Both the fragmentation reaction (1a) and the methylenecyclopropane rearrangement (1b) were observed under these conditions.



(1)

In view of the extended chromophoric systems that these reactants contained, very little information concerning the identity of the excited state(s) that was (were) involved can be obtained. In the first study of a methylenecyclopropane without conjugating groups, Gilbert and Luo[6] photolyzed **1** with radiation >200 nm and showed that it fragmented to cyclooctene and dimethylvinylidene $(CH_3)_2C{=}C{:}$, the latter being identified by either trapping with cyclohexene or by the isolation of its rearrangement product.



1 **2** **3**

These results will be discussed later in this article. A key result on the photolysis of a monocyclic methylenecyclopropane was reported by Takeda et al.[7] They found that irradiation of methylenecyclopropane itself in a low-temperature matrix with "ultraviolet light" (presumably radiation >200 nm) did not lead to the ESR spectrum of trimethylenemethane in its triplet ground

* Address correspondence to this author at the IBM Thomas J. Watson Research Center.

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