Stereoselective O_2-induced photoisomerization of all-*trans*-1,6-diphenyl-1,3,5-hexatriene

Jack Saltiel, Govindarajan Krishnamoorthy, Zhennian Huang, Dong-Hoon Ko, and Shujun Wang

Abstract: Irradiation of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) in degassed acetonitrile (AN) gives *ctt*- and *tct*-DPH, relatively inefficiently, mainly via isomerization in the singlet excited state. The triplet contribution to the photoisomerization is small due to a very low intersystem crossing yield (ϕ_{is} = 0.01). Central bond isomerization is quenched in the presence of air by a factor of 1.4, consistent with the expected quenching of the lowest singlet and triplet excited states by oxygen. However, the presence of air enhances terminal bond photoisomerization by nearly twofold. Triplet-sensitized *ttt*-DPH photoisomerization favors *tct*-DPH formation and is quenched by oxygen. It follows that the interaction of singlet-excited *ttt*-DPH with O_2 suppresses isomerization to *tct*-DPH but opens a new isomerization pathway to *ctt*-DPH. The presence of dimethylfuran, a singlet O_2 trap, has no effect on the photoisomerization, eliminating the possible involvement of singlet O_2 in this new reaction. *ttt*-DPH radical cations are ruled out as intermediates because the presence of fumaronitrile, which leads to their formation, suppresses both central and terminal bond photoisomerizations. In contrast to acetonitrile, *ctt*-DPH formation is quenched by oxygen in methylcyclohexane, suggesting the requirement of a polar environment. Strikingly different deuterium isotope effects distinguish the direct and O_2-induced photoisomerization pathways. A comparative study of *ttt*-DPH-d_0 with *ttt*-DPH-d_2 and *ttt*-DPH-d_4, involving deuteration of one and both terminal double bonds, reveals an inverse kinetic isotope effect (k_H^{ox}/k_D^{ox} = 0.92) for the O_2-induced reaction. An attractive mechanism for the new oxygen-induced photoisomerization involves charge transfer from the S_1 state of *ttt*-DPH to oxygen followed by collapse of the exciplex to either a zwitterionic or a biradicaloid species through bonding at one of the benzylic positions. Rotation about the new single bond in this intermediate followed by reversion to DPH and O_2 gives the observed result.

Key words: diphenylhexatrienes, trans-cis photoisomerization, oxygen sensitization.

Résumé : L'irradiation du 1,6-diphénylhexa-1,3,5-triène complètement *trans* (*ttt*-DPH), dans de l'acétonitrile dégazé (AN) conduit d'une façon relativement inefficace à la formation des *ctt*- et *tct*-DPH, principalement par le biais d'une isomérisation dans l'état excité singulet. La contribution triplet à la photoisomérisation est faible en raison du très faible rendement du passage intersystème (ϕ_{is} = 0,01). L'isomérisation de la liaison centrale est piégée en présence d'air par un facteur de 1,4 qui est en accord le piégeage par l'oxygène des états excités singulet et triplet les plus bas. Toutefois, la présence d'air augmente la photoisomérisation de la liaison terminale par un facteur égal pratiquement à deux. La photoisomérisation du *ttt*-DPH sensibilisée au niveau triplet favorise la formation de *tct*-DPH et elle est piégée par l'oxygène. Il en découle que l'interaction de l'oxygène avec le *ttt*-DPH excité à l'état singulet supprime l'isomérisation en *tct*-DPH mais qu'elle conduit à une nouvelle voie d'isomérisation conduisant au *ctt*-DPH. La présence de diméthylfurane, un piège pour O_2 à l'état singulet, n'a pas d'effet sur la photoisomérisation ce qui élimine la possibilité d'implication du O_2 à l'état singulet dans cette nouvelle réaction. On a éliminé la possibilité d'une implication des cations radicaux *ttt*-DPH comme intermédiaires sur la base du fait que la présence de fumaronitrile qui conduit à leur formation supprime les photoisomérisations des liaisons tant terminale que centrale. Par opposition à ce qui est observé avec l'acétonitrile, la formation de *ctt*-DPH est piégée par l'oxygène dans le méthylcyclohexane ce qui suggère la nécessité d'un environnement polaire. Des effets isotopiques du deutérium très différents distinguent les voies de photoisomérisations directe et induite par O_2. Une étude comparative des *ttt*-DPH-d_0, *ttt*-DPH-d_2 et *ttt*-DPH-d_4 impliquant la deutération d'une et des deux doubles liaisons terminales permet de mettre en évidence un effet isotopique cinétique inverse, k_H^{ox}/k_D^{ox} = 0,92, pour la réaction induite par O_2. Un mécanisme intéressant pour la nouvelle photoisomérisation induite par l'oxygène implique un transfert de charge de l'état S_1 du *ttt*-DPH vers l'oxygène, suivi d'une décomposition de l'exciplex en espèces soit zwitterionique ou biradicaloïde par le biais de la formation d'une liaison à l'une des positions benzyliques. Une rotation autour de la nouvelle liaison simple de cette intermédiaire, suivie d'une

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Dedicated to Professor Don Arnold for his contributions to chemistry.

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réversion en DPH et en O_2, conduit au résultat observé.

Mots clés : diphénylhexatriènes, photoisomérisation trans-cis, sensibilisation par l'oxygène.

[Traduit par la Rédaction]

Introduction

all-*trans*-1,6-Diphenyl-1,3,5-hexatriene (*ttt*-DPH) has been used as a model for the long polyenes related to the retinols and vitamin A. It is the first member of the α,ω-diphenylpolyene vinylogous family whose all-s-trans conformer exhibits fluorescence both from the initially excited 1 ^1B_u state and from a lower energy singlet excited state that, following Hudson and Kohler, is identified as the forbidden doubly excited 2 ^1A_g state (1–3). The lowest singlet excited states of all longer diphenylpolyenes (1–3) and of all conjugated polyenes starting with 1,3-butadiene (4–7), have also been identified as 2 ^1A_g states. In degassed solutions the trans → cis photoisomerization of *ttt*-DPH following direct excitation occurs inefficiently by a combination of singlet and triplet pathways (8). In the triplet state, the ground state isomers of DPH exist as a mixture of freely equilibrating conformers in which ttt, tct, and ctt geometries dominate (9). In the absence of oxygen, triplet excitation transfer events between relatively long-lived DPH triplets and DPH ground states of different geometry are links in quantum chain processes that enhance the contribution of triplets to the photoisomerization, compensating somewhat for the low intersystem crossing yields. The quenching of the triplets by oxygen significantly decreases their lifetime and prevents their participation in quantum chain events (9).

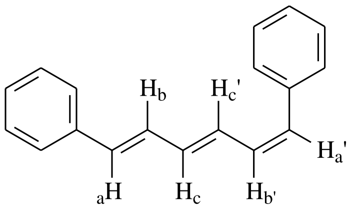
Changing the solvent from methylcyclohexane (MCH) to acetonitrile (AN) increases the rates of photoisomerization in the singlet excited state manifold, the increase being especially pronounced (20-fold) at the terminal double bonds (8, 10), thereby decreasing the singlet excited state lifetime and the contribution of the competing decay channels of fluorescence (ϕ_f = 0.65 and 0.27 at 20°C in MCH (11) and AN (10), respectively) and intersystem crossing (ϕ_{is} = 0.029 and 0.010 at 20°C in MCH (12) and AN (13, 14), respectively). Photoisomerization in the ttt → ctt direction in AN is almost entirely a singlet excited state process (98%) that is attenuated by a factor of 1.36 on deuteration of the olefinic hydrogens of the terminal double bond (10).

We report here the effect of oxygen on the photoisomerization of *ttt*-DPH and its 1,2-dideuterio and 1,2,5,6-tetradeuterio derivatives upon direct excitation in AN. In contrast to the central bond whose photoisomerization is attenuated, consistent with oxygen quenching of singlet and triplet excited states, oxygen enhances photoisomerization at the terminal double bonds. The mechanism of this new photoisomerization pathway is addressed in this paper.

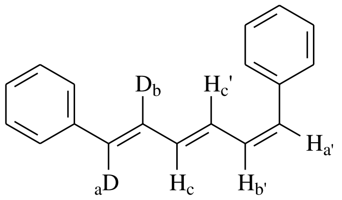
Experimental section

Materials

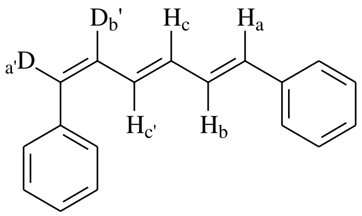
Sources and purification procedures for all-*trans*-1,6-diphenyl-1,3,5-hexatriene (100.0%, HPLC), benzophenone, *trans*-stilbene, anthracene, and acetonitrile have been described (8, 10). Acetonitrile was used as received or purified using a known procedure (15). Lithium perchlorate (Spectrum, anhydrous ACS reagent) was used as received. The syntheses of 1,2-dideuterio- (*ttt*-DPH-d_2, 99.9%, HPLC) and 1,2,5,6-tetradeuterio-all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH-d_4, 98.0%, HPLC, 1.7% *tcc*-DPH-d_4, major contaminant) have been described (10). Prior to use in this study, *ttt*-DPH-d_4 was recrystallized three times to a final purity of 99.4% with 0.5% *tcc*-DPH-d_4, the major contaminant.



ttc-DPH-d_0



ttc-DPH-d_2



ctt-DPH-d_2

Irradiation procedure

Irradiations were carried out in a Moses merry-go-round (16) apparatus immersed in a thermostated water bath. A heating coil connected to a thermoregulator (Polyscience Corporation) was used to control the temperature to 20 ± 0.1°C. The benzophenone-sensitized photoisomerization of *trans*-stilbene was used for actinometry ($\phi_{t\rightarrow c}$ = 0.55) (17, 18). A Hanovia medium pressure Hg lamp (200 W, Ace Glass, Inc.) and Corning CS 7-37 and 0-52 filters were used for excitation at 366 nm. Aliquots of actinometer solutions (3.0 mL) were pipetted into Pyrex ampoules (13 mm o.d.), degassed, and flame-sealed at a constriction. Air-saturated DPH solutions (1.0×10^{-3} M in AN, 3 mL aliquots) were irradiated in 13 mm o.d. Pyrex ampoules lightly stoppered with Teflon-tape-covered rubber stoppers. In some instances, the ampoules were provided with fritted disks at the bottom for bubbling air or oxygen throughout the irradiation. Sample preparation, degassing, and analysis were performed in almost complete darkness (red light).

Analytical procedures

Actinometer solutions were analyzed by GLC and DPH solutions by HPLC (λ_{mon} = 350 nm) as previously described (8, 9), except that on replacing AN with hexanes prior to HPLC analyses, a stream of argon was used to evaporate the solvent and care was exercised to avoid taking samples to dryness (10). This procedure minimizes *ctt*-DPH losses.

Fluorescence measurements

Fluorescence *spectra* were measured with a Hitachi/PerkinElmer MPF-2A fluorescence spectrophotometer as previously described (19), or with a Hitachi F4500 fluorimeter. Fluorescence spectra were recorded for both air-saturated and Ar-bubbled solutions of DPH in AN in standard 1 cm^2 quartz cells. Temperature was maintained at 20.0 ± 0.1°C using a Neslab-RTE 4DD constant temperature circulation bath, and was monitored continuously during each scan with an Omega Engineering Model 199 RTD digital thermometer in a reference cell placed in the same constant temperature cell holder. Fluorescence *lifetimes* were measured with a phase modulation Fluorolog-τ2 lifetime spectrofluorometer (SPEX) equipped with a 450 W Xe arc source, a Hamamatsu R928P photomultiplier tube, and a Lasermetrics BNC1072FW Pockel cell (KD_2PO_4). The Fluorolog-τ2 modulates the frequency of the excitation light from 0.5 to 300 MHz. A glycogen solution (τ = 0 ns, scattered light) was used as reference. Temperature was maintained at 20.0 ± 0.1°C and was monitored continuously during each scan as described above. Air-saturated *ttt*-DPH solutions (2.0×10^{-6} M) were employed. Software (DMF 3000F Spectroscopy) provided by the manufacturer was used to analyze the data. Determinations of the quality of the lifetimes were based on examination of the statistics of the fit (a plot of the residual deviations vs. frequency) and reduced χ^2 values that were all close to unity.

Results

Photochemical observations

Photostationary states were approached from the *ttt*-DPH-d_n (n = 2 and 4) side. Degassed DPH samples (1.0×10^{-3} M) in air-saturated AN were irradiated for different time intervals at 20.0°C until HPLC analysis revealed no further change in the isomer composition. Photostationary state fractions are shown in Table 1. Overall conversions for quantum yield measurements were kept below 8% and were corrected for back reaction as has been described (10). Quantum yields are also shown in Table 1. The effect of additives was studied for *ttt*-DPH-d_0. The presence of up to 0.40 M $LiClO_4$ had no effect on ctt/tct conversion ratios for both air-saturated and degassed AN solutions. The presence of 0.188 M 2,5-dimethylfuran (DMF) had no significant effect on photoisomerization quantum yields of 1.38×10^{-3} M *ttt*-DPH-d_0 in air-saturated AN. Similarly, addition of up to 1.2×10^{-3} M diethylamine (DEA) to 1.00×10^{-3} M *ttt*-DPH-d_0 in degassed or air-saturated AN solutions did not alter the photoisomerization quantum yields.

Table 1. PSS fractions and photoisomerization quantum yields for *ttt*-DPH-d_n in air-saturated AN (366 nm, 20.0°C).[a]

DPH	ctt + ttc	tct	ttt
PSS fractions			
d_0	0.430(0.239)	0.095(0.106)	0.400(0.635)
d_2	0.419(0.206)	0.100(0.106)	0.401(0.667)
d_4	0.395(0.183)	0.109(0.115)	0.402(0.661)
Quantum yields	$\phi_{ctt+ttc}$	ϕ_{tct}	
d_0	0.121 (0.062)	0.025 (0.035)	
d_2	0.119 (0.054)	0.026 (0.036)	
d_4	0.114 (0.046)	0.028 (0.038)	

[a] Values in parentheses are corresponding values under degassed conditions from ref. (10); estimated uncertainties in absolute quantum yields are ±5%.

Fluorescence measurements

The fluorescence of 1.0×10^{-3} *M* *ttt*-DPH-d_0 in degassed and air-saturated AN was found to be independent of [DEA] up to 1.5×10^{-3} M. Fluorescence lifetimes at different temperatures for air-saturated solutions are compared in Table 2 with those for degassed solutions (10). Excellent fits to the single exponential decay model were obtained ($\chi^2 \leq 1.2$) and the lifetimes were independent of excitation and monitoring wavelengths, within experimental uncertainty. Reproducibility in independent measurements was better than ±0.1 ns.

Discussion

Background

The ground state of molecular oxygen is generally a very effective quencher of electronically excited molecules (20). Rate constants for oxygen quenching of singlet excited states of aromatic hydrocarbons in hydrocarbon solvents are often close to the diffusion-controlled limit. Corresponding values for triplet state quenching are usually an order of magnitude smaller owing to restrictions by spin statistical factors (20–22). These quenching events are commonly associated with formation of the lowest singlet state of the oxygen molecule $O_2^*(^1\Delta_g)$, sometimes through the intermediacy of the higher energy state $O_2^*(^1\Sigma_g^+)$. In the case of singlet excited states of aromatic hydrocarbons, induced intersystem crossing has been shown to accompany oxygen quenching in hydrocarbon media (23), a pathway to triplets that is diminished by polar solvents such as acetonitrile (23–25). The importance of a charge transfer (CT) quenching pathway by oxygen was first established by Kikuchi et al. (26) who showed that, for anthracenecarbonitriles and acridinium salts, fluorescence quenching rate constants in acetonitrile decrease as the free energy for full electron transfer (ΔG_S^{CT}) increases from negative to positive values. A comprehensive systematic study of the contribution of CT in the quenching of aromatic hydrocarbon singlet and triplet states by oxygen in AN was described by Abdel-Shafi and Wilkinson (27). With the exception of tetracene that undergoes significant chemical degradation, the net rate constants for the triplet quenching

Table 2. O_2 effect on *ttt*-DPH-d_0 fluorescence lifetimes (366 nm).[a]

T (°C)	τ (Air, ns)	τ (Deg, ns)[b]
10.0	3.9	5.3
20.0	3.5	4.7
30.0	2.9	4.1
40.0	2.5	3.6
50.0	2.2	3.2

[a] Reproducibility in independent measurements was better than ±0.1 ns.

[b] From ref. (10).

pathway involving CT were shown to correlate well with ΔG_T^{CT}, indicating a transition state with 13.5% CT character (27). Net rate constants for the analogous process involving excited singlet states were as high as 1.6×10^{10} M^{-1} s^{-1} but could not be determined over a sufficiently large ΔG_S^{CT} range to establish a meaningful logarithmic dependence on this quantity (27). Except in the case of 2,6-dimethoxynaphthalene (DMN) for which the quenching event is accompanied by a small yield of ^{2}DMN$^{\cdot+}$ (3×10^{-3}) (25), attempts to detect the radical cations of the donors and $^{2}O_2^{\cdot-}$ have failed, despite the exothermicity of full electron transfer in AN for most of the excited singlet donors studied (25, 27).

Energy transfer from the triplet state of *ttt*-DPH to O_2 in air-saturated solutions yields $O_2^*(^1\Delta_g)$ with unit efficiency (28). Quenching of the singlet state of *ttt*-DPH leads to $O_2^*(^1\Delta_g)$ less efficiently and the efficiency decreases with increasing solvent polarity (0.5 and 0.3 in cyclohexane and methanol, respectively) (29). Competing with $O_2^*(^1\Delta_g)$ formation is O_2-induced intersystem crossing leading to as much as a 10-fold increase in ϕ_{is} (0.015 to 0.15 for degassed vs. air-saturated methanol (12)).

Two-photon laser excitation of *ttt*-DPH gives the radical cation (^{2}*ttt*-DPH$^{\cdot+}$) in a variety of solvents (30, 31). In AN the lifetime of the radical cation (7.3 μs) is insensitive to the presence of air (31, 32). The radical cation is also observed on quenching of ^{1}*ttt*-DPH* by electron acceptors in polar solvents including AN (12, 13). It isomerizes to a new transient, assigned as a product of trans → cis photoisomerization, which reverts thermally to ^{2}*ttt*-DPH$^{\cdot+}$, and reacts efficiently with electron donors to give back the starting *ttt*-DPH (31).

Oxygen effects on *ttt*-DPH photoisomerization

We reported earlier that the fluorescence quantum yields and lifetimes of *ttt*-DPH-d_n (n = 0, 2, and 4) in AN are nearly independent of deuterium substitution at the terminal double bonds (10). It was not surprising, therefore, that oxygen in air-saturated AN solutions at 20°C attenuates fluorescence quantum yields and lifetimes of the three *ttt*-DPH-d_n (n = 0, 2, and 4) by the same 1.31 ± 0.01 factor, within experimental uncertainty (10). The 1.3_4 ratio of the lifetimes at 20°C in Table 2 is in reasonable agreement with the quantum yield measurements and the effect is similar at different temperatures. Use of $1.9 \pm 0.2 \times 10^{-3}$ for the oxygen concentration in air-saturated AN (33) gives $k_{qox} = (3.5 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1} for the quenching of the excited singlet states of *ttt*-DPH-d_n (n = 0, 2, and 4) by molecular oxygen, a value close to the diffusion-controlled limit.

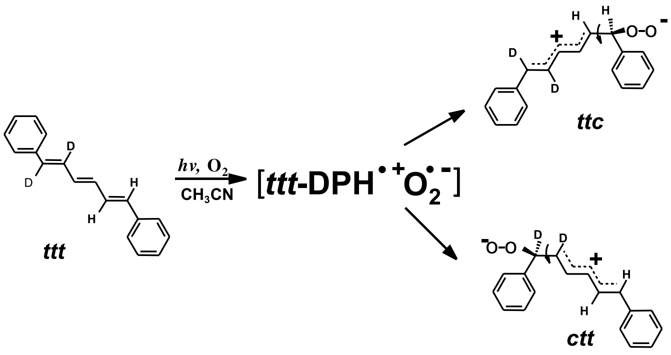
The range of attenuations of $\phi_{ttt \to tct}$ values by oxygen is slightly larger (1.36 to 1.40) than the attenuations of fluorescence quantum yields and lifetimes, because in addition to quenching the singlet excited state, oxygen dramatically shortens the lifetime of DPH triplets, effectively eliminating quantum chain contributions to the photoisomerization (9*b*). Oxygen interferes with the photoisomerization of the central bond of *ttt*-DPH-d_n (n = 0, 2, and 4) only in so far as it deactivates *ttt*-DPH-d_n excited singlet (primarily) and triplet states. Photoisomerization quantum yields in the presence of FN in degassed and air-saturated AN solutions are consistent with an O_2 induced sixfold (compared with factors of 7 and 10 reported for cyclohexane and methanol, respectively, (12, 29)) enhancement of ϕ_{is} (34). In this case, however, this is a minor perturbation because it only raises ϕ_{is} from 0.01 to 0.06.

The results in Table 1 reveal a strikingly different O_2 effect on terminal bond photoisomerization. Instead of the expected ~1.3-fold attenuation, ϕ_{ctt} values are enhanced by factors of 2 to 2.5, progressively increasing with terminal bond deuteration. Correspondingly, the presence of air strongly shifts photostationary state (PSS) compositions to larger *ctt*-DPH contributions at the expense of *ttt*-DPH. Oxygen enhanced *trans* to *cis* 1,2-diarylethene photoisomerization quantum yields have previously been observed, but were generally attributed to O_2 induced intersystem crossing (35–38). For instance, in the case of *trans*-4,4′-diphenylstilbene, quenching of the highly fluorescent singlet excited state by ~1×10^{-2} M O_2 in methylcyclohexane increases $\phi_{t \to c}$ 18-fold from 0.0025 to 0.045. However, because DPH triplets in AN favor decay to *tct*-DPH over decay to *ctt*-DPH by at least a factor of 5 (9*a*), O_2-catalyzed intersystem crossing would be expected to increase ϕ_{tct} more than ϕ_{ctt}. Instead, we observe enhancement of the latter and quenching of the former. We conclude that the differential O_2 effects on central and terminal bond photoisomerization rule out the O_2-induced intersystem crossing pathway in *ttt*-DPH.

In the *Background section*, we reviewed evidence for the formation of radical cations (^{2}*ttt*-DPH$^{\cdot+}$) in AN solutions. We recently evaluated and ruled out their possible involvement in the photoisomerization of *ttt*-DPH following direct excitation in degassed AN (8). Briefly, fluorescence and photoisomerization quantum yields, measured as a function of fumaronitrile (FN) concentration, show that ^{2}*ttt*-DPH$^{\cdot+}$ radical cations formed from the ^{1}(*ttt*-DPH–FN)* exciplex (13) undergo no photoisomerization (8). It is not surprising, therefore, that we find that addition of up to 0.015 M diethylamine (DEA) has no effect on the photoisomerization quantum yields and, in particular, on the ϕ_{ctt}:ϕ_{tct} ratio in either degassed or air-saturated AN. At the high concentrations employed, DEA, a known, effective quencher of ^{2}*ttt*-DPH$^{\cdot+}$ radical cations, $k_q = 1.05 \times 10^9$ M^{-1} s^{-1} (31*a*), should have intercepted them all, in view of their long lifetime (7.3 μs) (31). In the unlikely event that electron transfer from ^{1}*ttt*-DPH* to O_2 contributes to the formation of ^{2}*ttt*-DPH$^{\cdot+}$ radical cations, they are not involved in *trans* → *cis* photoisomerization.

The possibility that O_2 opens a thermal free radical isomerization process can be ruled out because the observed

Scheme 1.



formation of more cis double bonds moves the system up hill thermodynamically (9*b*). We are left with addition followed by elimination starting from ^{1}*ttt*-DPH*–O_2 interaction, as a viable Schenck-type mechanism (39) for the O_2-induced photoisomerization (Scheme 1). Although the adduct (adducts for *ttt*-DPH-d_2) in Scheme 1 is shown as a zwitterionic species because this process is much more pronounced in AN than in MCH,[2] the possibility that the adduct is biradicaloid cannot be ruled out. Bond formation at the benzylic positions should be favored because it leads to the more delocalized carbon-centered cation or radical intermediate. Rotation about the new single bond followed by loss of O_2 would explain enhanced *ctt*-DPH formation. In principle, the intermediate could form either from the interaction of ^{1}*ttt*-DPH* with ground state O_2 ($^3\Sigma_g$) or by the addition of singlet $^1O_2$* ($^1\Delta_g$) to ground state *ttt*-DPH. However, if $^1O_2$* were responsible for enhanced values under direct excitation conditions, then O_2 would enhance ϕ_{ctt} values even more under triplet-sensitized conditions because the efficiency of $^1O_2$* formation is higher when ^{3}*ttt*-DPH* is quenched by $^3O_2$ (28, 29). It follows that the involvement of $^1O_2$* can be ruled out because we have found no photoisomerization enhancement of any kind under triplet-sensitized conditions in air-saturated AN (9). As a further precaution, we now report that addition of 0.188 M 2,5-dimethylfuran (DMF), a very efficient $^1O_2$* scavenger (28, 41), has no effect on the ϕ_{ctt}:ϕ_{tct} ratio in air-saturated AN.

Table 3. Dissection of quantum yields for terminal bond photoisomerization into normal and oxygen pathways.

DPH	$(1 - f_{ox})$	$\phi_{ctt+ttc}^{S}$	$\phi_{ctt+ttc}^{ox}$	k_H^{ox}/k_D^{ox}	f_{ad}
d_0	0.76_2	0.047	0.074		0.62
d_2	0.75_9	0.041	0.078	0.90	0.65
d_4	0.75_9	0.035	0.079	0.94	0.66

Deuterium isotope effect

The small increasing trend in ϕ_{tct} values under both degassed and air-saturated conditions with increasing deuterium substitution is consistent with the effect of deuterium on the lifetime of ^{1}*ttt*-DPH* (10). Terminal bond deuterium substitution does not affect rate constants for central bond isomerization. In contrast, ϕ_{ctt} values decrease strongly in degassed solutions and show a less-pronounced decrease in the presence of air. The torsional relaxation rate constants for dihydro- and dideuterio-terminal bonds in ^{1}*ttt*-DPH* are subject to a normal deuterium isotope effect (k_H/k_D = 1.36) (10). Analysis of ϕ_{ctt} values in the presence of air is accomplished by dissecting them into contributions from the normal pathway, involving the fraction of ^{1}*ttt*-DPH* not intercepted by oxygen ($1 - f_{ox}$), and the new pathway, involving the fraction of ^{1}*ttt*-DPH* that is intercepted by oxygen (f_{ox}) and follows the pathway in Scheme1. Since nearly all terminal bond isomerization in degassed solution is a singlet excited state reaction, we expect that, in the presence of air, the normal pathway will experience the same attenuation as fluorescence. Substitution of $k_{qox} = 3.5 \times 10^{10}$ M^{-1} s^{-1} for the quenching of the excited singlet states of *ttt*-DPH-d_n (n = 0, 2, and 4), $[O_2] = 1.9 \times 10^{-3}$ M, and the singlet excited state lifetimes (τ_f^0) (10) in eq. [1] gives the ($1 - f_{ox}$) values listed in

$$[1] \qquad (1 - f_{ox}) = k_{qox}\tau_f^0[O_2]/(1 + k_{qox}\tau_f^0[O_2])$$

Table 3. Quantum yields for terminal bond isomerization by the normal singlet excited state pathway ($\phi_{ctt\,+\,ttc}^{S}$) obtained by multiplying the values under degassed conditions (given in parentheses in Table 1) by the ($1 - f_{ox}$) attenuation factors, were subtracted from observed quantum yields in the presence of air to obtain $\phi_{ctt\,+\,ttc}^{ox}$, the quantum yields for the O_2-induced pathway (Table 3). Assuming that Scheme 1 applies, the ratio of the rate constant for bond formation at a benzylic position bearing hydrogen (k_H^{ox}), to the analogous rate constant for a benzylic position bearing deuterium (k_D^{ox}) is given by

$$[2] \qquad k_H^{ox}/k_D^{ox} = (\alpha_D/\alpha_H)(\phi_{ctt}^{d0}/\phi_{ctt}^{d4})(\tau_{d4}^{ox}/\tau_{d0}^{\ ox})$$

where the αs are decay fractions to *ctt*-DPH for the deuterated and undeuterated DPH–O_2 adducts, the quantum yields are the values for the O_2-induced pathway from Table 3, and the fluorescence lifetimes are in the presence of air. Taking $\alpha_D = \alpha_H$ and substituting for the other quantities in eq. [2] using the data for *ttt*-DPH-d_0 and *ttt*-DPH-d_4 gives k_H^{ox}/k_D^{ox} = 0.94. This requires that formation of the DPH–O_2 exciplex be somewhat reversible, as no intermolecular deuterium isotope effect would be expected if exciplex formation were irreversible and product determining. A similar treatment using the data for *ttt*-DPH-d_0 and *ttt*-DPH-d_2 gives k_H^{ox}/k_D^{ox} = 0.90. The inverse secondary deuterium isotope effect is consistent with the expected sp^2 to sp^3 rehybridization in the transition states leading to the adducts (42, 43).

Significant fractions of ^{1}*ttt*-DPH*–O_2 quenching interactions must follow the adduct pathway to isomerization. These fractions (f_{ad}) can be estimated from $f_{ox}/(\alpha\phi_{ctt\,+\,ttc}^{ox})$ by assuming equal partitioning of the adducts to cis and trans double bonds (α = 0.5). The resulting values are rela-

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[2] In MCH, the presence of air attenuates *tct*- and *ctt*-DPH formation by factors of 0.35 and 0.58, respectively (34, 40).

tively insensitive to deuterium substitution falling in a narrow 0.62 to 0.66 range (Table 3).

Trapping the exciplex

Initial indications that the O_2-induced photoisomerization pathway is quenched when $Li^+ClO_4^-$ is included in AN (34), were not confirmed when great care was taken to avoid *ctt*-DPH loss in sample preparation for HPLC analysis. Because no changes in $\phi_{ctt}:\phi_{tct}$ ratios were observed even when a saturated $Li^+ClO_4^-$ solution (~0.4 M) was used in air-saturated AN, we can conclude that Li^+ fails to intercept an ion pair in this case. This approach has been shown to succeed in several instances (44). Apparently, in our case, either charge transfer is not complete in the exciplex, or the exciplex is too short-lived. An interesting anomaly is our preliminary observation that on attempting to increase the contribution of the O_2-induced photoisomerization pathway by increasing the O_2 concentration (bubbling O_2 during the irradiation) we were surprised to find lower $\phi_{ctt}:\phi_{tct}$ ratios than in the presence of air. If the mechanism in Scheme 1 is correct, this result suggests that, at the higher concentration, oxygen quenches the *ttt*-DPH–O_2 exciplex. While oxygen quenching of singlet exciplexes is well-known (45), quenching of an oxciplex is unprecedented and remains to be established.

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References

1. B.S. Hudson and B.E. Kohler. Annu. Rev. Phys. Chem. **25**, 437 (1974).
2. B.S. Hudson, B.E. Kohler, and K. Schulten. *In* Excited states. Vol. 6. *Edited by* E.C. Lim. Academic Press, New York. 1982. pp. 1–95.
3. J. Saltiel and Y.-P. Sun. *In* Photochromism, molecules and systems. *Edited by* H. Dürr and H. Bouas-Laurent. Elsevier, Amsterdam. 1990. pp. 64–164.
4. W. Fuß, S. Lochbrunner, W.E. Schmid, and K.L. Kompa. J. Phys. Chem. A, **102**, 9334 (1998).
5. W. Fuß, W.E. Schmid, and S.A. Trushin. J. Chem. Phys. **112**, 8347 (2000).
6. For a recent review of polyene photophysics, see: W. Fuß, Y. Haas, and S. Zilberg. Chem. Phys. **259**, 273 (2000).
7. (*a*) S.H. Pullen, N.A. Anderson, L.A. Walker, II, and R.J. Sension. J. Chem. Phys. **108**, 556 (1998); (*b*) N.A. Anderson, J.J. Shiang, and R.J. Sension. J. Phys. Chem. A, **103**, 10 730 (1999).
8. J. Saltiel, S. Wang, L.P. Watkins, and D.-H. Ko. J. Phys. Chem. A, **104**, 11 443 (2000).
9. (*a*) J. Saltiel, S. Wang, D.-H. Ko, and D.A. Gormin. J. Phys. Chem. A, **102**, 5383 (1998); (*b*) J. Saltiel, J.M. Crowder, and S. Wang. J. Am. Chem. Soc. **121**, 895 (1999).
10. J. Saltiel, G. Krishnamoorthy, Z. Huang, D.-H. Ko, and S. Wang. J. Phys. Chem. A, **107**, 3178 (2003).
11. E.D. Cehelnik, R.B. Cundall, J.R. Lockwood, and T.J. Palmer. J. Phys. Chem. **79**, 1369 (1975).
12. S.K. Chattopadhyay, P.K. Das, and G.L. Hug. J. Am. Chem. Soc. **104**, 4507 (1982).
13. F.W. Schael. Ph.D. Dissertation, Technische Universität, Carlo-Wilhelmina zu Braunschweig, Germany, 1995.
14. (*a*) F.W. Schael and H.-G. Löhmannsröben. Chem. Phys. **206**, 193 (1996); (*b*) F.W. Schael, J. Kühster, and H.-G. Löhmannsröben. Chem. Phys. **218**, 175 (1997). (*c*) F.W. Schael and H.-G. Löhmannsröben. J. Photochem. Photobiol. A, **105**, 317 (1997).
15. J.F. O'Donnel, J.T. Ayres, and C.K. Mann. Anal. Chem. **37**, 1161 (1965).
16. F.G. Moses, R.S.H. Liu, and B.M. Monroe. Mol. Photochem. **1**, 245 (1969).
17. H.A. Hammond, D.E. DeMeyer, and J.L.R. Williams. J. Am. Chem. Soc. **91**, 5180 (1969).
18. D. Valentine, Jr. and G.S. Hammond. J. Am. Chem. Soc. **94**, 3449 (1972).
19. J. Saltiel, D.F. Sears, Jr., J.-O. Choi, Y.-P. Sun, and D.W. Eaker. J. Phys. Chem. **98**, 35 (1994); **98**, 8260 (1994).
20. (*a*) I.B. Berlman. Handbook of fluorescence spectra of aromatic molecules. 2nd ed. Academic Press, New York. 1971; (*b*) J. Saltiel and B.W. Atwater. Adv. Photochem. **14**, 1 (1988); (*c*) F. Wilkinson, W.P. Helman, and A.B. Ross. J. Phys. Chem. Ref. Data, **22**, 113 (1993).
21. (*a*) G. Porter and M.R. Wright. Discuss. Faraday Soc. **27**, 18 (1959); (*b*) B. Stevens and B.E. Algar. Ann. N. Y. Acad. Sci. **171**, 50 (1970).
22. O.L.J. Gijzeman, F. Kaufman, and G. Porter. J. Chem. Soc., Faraday Trans. 2, **69**, 708 (1973).
23. R. Potashnik, C.R. Goldschmidt, and M. Ottolenghi. Chem. Phys. Lett. **9**, 424 (1971).
24. (*a*) F. Wilkinson, D.J. McGarvey, and A.F. Olea. J. Am. Chem. Soc. **115**, 12 144 (1993); (*b*) A.F. Olea and F. Wilkinson. J. Phys. Chem. **99**, 4518 (1995).
25. C. Sato, K. Kikuchi, C. Sato, Y. Takahashi, and T. Miyashi. J. Phys. Chem. **99**, 16 925 (1995).
26. K. Kikuchi, K. Okamura, M. Watabe, H. Ikeda, Y. Takahashi, and T. Miyashi. J. Am. Chem. Soc. **115**, 5180 (1993).
27. A.A. Abdel-Shafi and F. Wilkinson. J. Phys. Chem. A, **104**, 5747 (2000).
28. K.C. Wu and A.M. Trozzolo. J. Phys. Chem. **83**, 3180 (1979).
29. S.K. Chattopadhyay, C.V. Kumar, and P.K. Das. J. Phys. Chem. **89**, 670 (1985).
30. M. Almgren and J.K. Thomas. Photochem. Photobiol. **31**, 329 (1980).
31. (*a*) Z. Wang and W.G. McGimpsey. J. Phys. Chem. **97**, 3324 (1993); (*b*) Z. Wang and W.G. McGimpsey. J. Phys. Chem. **97**, 5054 (1993).
32. H. Görner. J. Photochem. **19**, 343 (1982).
33. W.D.K. Clark and C. Steel. J. Am. Chem. Soc. **93**, 6347 (1971).
34. S. Wang. Ph.D. Dissertation, Florida State University, Tallahassee, Florida, 1998.
35. P. Bortolus and G. Galiazzo. J. Photochem. **2**, 361 (1974).
36. G. Fischer and E. Fischer. Mol. Photochem. **6**, 463 (1974).
37. G.G. Aloisi, U. Mazzucato, J.B. Birks, and L. Minuti. J. Am. Chem. Soc. **99**, 6340 (1977).
38. For a review see: J. Saltiel, J.L. Charlton. *In* Rearrangements in ground and excited states. Vol. 3. *Edited by* P. de Mayo. Academic Press, New York. 1980. Essay 14.
39. G.O. Schenck and R. Steinmetz. Bull. Soc. Chim. Belg. **71**, 781 (1962).
40. D.-H. Ko. Ph.D. Dissertation, Florida State University, Tallahassee, Florida, 1997.

41. K. Gollnick, T. Franken, G. Schade, and G. Dorhofer. Ann. N.Y. Acad. Sci. **171**, 89 (1970).
42. A. Streitwieser, Jr., R.H. Jagow, R.C. Fahey, and S. Suzuki. J. Am. Chem. Soc. **80**, 2326 (1958).
43. For relevant early examples, see: M. Matsuoka and M. Szwarc. J. Am. Chem. Soc. **83**, 1260 (1961).
44. (*a*) J. Gersdorf and J. Mattay. J. Photochem. **28**, 405 (1985); (*b*) M. Mac and J. Wirz. Chem. Phys. Lett. **211**, 20 (1993); (*c*) M. Mac, P. Kwiatkowski, and A.M. Turek. Chem. Phys. Lett. **250**, 104 (1996); (*d*) M. Mac and J. Wirz. Photochem. Photobiol. Sci. **1**, 24 (2002).
45. For a typical example, see: J.L. Charlton, D.E. Townsend, B.D. Watson, P. Shannon, J. Kowalewska, and J. Saltiel. J. Am. Chem. Soc. **99**, 5992 (1977).