phenylethanol, 134312-18-8; 1-[2-[(*p*-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethanol, 134312-19-9; dibenzofuran, 132-64-9; 1,2-diphenyl-1-[2-(phenyloxy)phenyl]ethanol, 134312-20-2; 1-(4-dibenzofuranyl)-1,2-diphenylethanol, 134312-21-3; 1-[5-methyl-2-[(*p*-methylphenyl)oxy]phenyl]-1,2-diphenylethene, 134312-22-4; 1,2-diphenyl-1-[2-(phenyloxy)phenyl]ethene, 134312-23-5; 1-[2-[(*p*-chlorophenyl)oxy]-5-methylphenyl]-1,2-diphenylethene, 134312-24-6; 1-(4-dibenzofuranyl)-1,2-diphenylethene, 134312-25-7.

Enone Photochemistry. Dynamic Properties of Triplet Excited States of Cyclic Conjugated Enones as Revealed by Transient Absorption Spectroscopy

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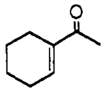
Abstract: Triplet π,π^* excited states of a large number of cyclic α,β-unsaturated ketones (enones) have been generated by pulsed laser excitation and detected by their characteristic ultraviolet absorption, λ_{max} 280–310 nm. The large variation in the lifetimes of these enone triplets as a function of molecular structure and the changes in rate constants for triplet energy transfer from enone triplets to naphthalene and methylnaphthalene for rigid vs nonrigid triplets are consistent with triplet relaxation by twisting around the olefinic bond. This has been confirmed by studies using time-resolved photoacoustic calorimetry (PAC), which afford both lifetimes and energies of the relaxed enone triplet states. The PAC lifetimes are in excellent agreement with those measured by transient absorption spectroscopy (TAS). The effect of substitution on the C=C bond on both lifetimes and energies of enone triplets is compatible with pyramidalization at the β-carbon atom of the triplet prior to intersystem crossing to the ground state. Rates of quenching by conjugated dienes are much lower than anticipated on consideration of the triplet energies of the enone as donor and the diene as acceptor. In systems in which enone–diene adducts are known to be formed, Stern–Volmer plots showed pronounced curvature. Self-quenching of enone triplets is particularly pronounced in the cases of cyclopentenone and some longer lived triplets but is not observed for simple cyclohexenones. In the latter case, the rate constant for self-quenching is too small to cause an unambiguous change in the short triplet lifetimes. The origin of the residual UV absorption observed for many enones following decay of the triplet has not been unambiguously established. Prominent candidates are dimeric triplet 1,4-biradicals en route to enone photodimers and deconjugated isomers of the starting enone.

Introduction

The photochemistry of cyclic enones has received much attention over the past 30 years, from mechanistic as well as synthetic perspectives.[1] The richness and complexity of this subject has been described in a recent review.[2] On the basis of classic sensitization and quenching studies, it was concluded that triplet states are exclusively responsible for the wide variety of photoreactions shown by these compounds, which include [2 + 2] cyclodimerization, reduction to saturated ketones and pinacols, molecular rearrangements, and [2 + 2] cycloaddition to alkenes.[1,2] Mechanistic investigations have frequently given ambiguous results. Some years ago we embarked on a program aimed at gaining a better understanding of the photoreactivity of cyclic enones as a function of variations in enone structure, by directly studying the dynamics of the various processes associated with radiationless decay of enone triplets using nanosecond flash photolysis.

The application of transient absorption spectroscopic (TAS) techniques to enone photochemistry was pioneered by Bonneau. His initial report[3] concerned 1-acetylcyclohexene (1-AC, **1**), which upon pulse excitation at either 265 or 353 nm produced two different transient absorptions. A species with maximum UV absorption at 280 nm appeared in less than 5 ns and decayed in about 20 ns, leading to a second species (lifetime 15 μs in acetonitrile or cyclohexane, 0.35 μs in methanol) with an absorption maximum at 345 nm. The short-lived transient absorption was assigned to a relaxed low-energy twisted triplet excited state of **1**, while the long-lived transient was suggested to be the ground-state trans isomer of **1**. The short lifetime of the triplet was attributed to facile intersystem crossing from the minimum on the triplet π,π^* (T_1) potential energy surface to the maximum on the ground state (S_0) surface, leading directly to the metastable *trans*-enone in competition with triplet decay to the *cis*-enone (**1**).[3]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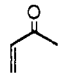
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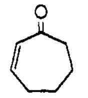
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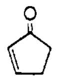
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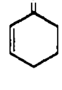
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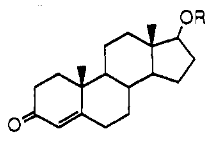

6 a, R = H
b, R = OCOCH$_3$

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Table I. Enone Triplet Lifetimes and Quenching Rate Constants Measured by Nanosecond Transient Absorption Spectroscopy

enone	solvent[a]	τ_{dir},[b,c] ns	τ_{extl},[d] ns	k_q, NA(MN), M^{-1} s^{-1}
2-cycloheptenone (**3**)	CH	11[e]		
1-acetylcyclohexene (**1**)	CH	16[e]		
2-cyclohexenone (**5**)	CH	25[e] (26)	29	7.5×10^8
	AN	23 (30)	24	1.0×10^9
	MeOH	27 (33)		
4,4-dimethylcyclohexenone (**7**)	AN	23 (28)	28	1.0×10^9
	CH	24 (23)		
	MeOH	40 (31)		
	t-BuOH	32	29	4.5×10^8
	IPA	21	28	8.5×10^8
4,4,6,6-tetramethyl-2-cyclohexenone (**11**)	AN	34		
octalone (**10**)	AN	57	58	(1.3×10^9)
	CH	47		
2-methylcyclohexenone	AN	51	83	(5.2×10^9)
3-methylcyclohexenone	AN	75	69	(4.6×10^9)
	CH	62	(187)[f]	(1.5×10^{10})
3-ethylcyclohexenone	AN	68	63	(1.1×10^9)
2,3-dimethylcyclohexenone	AN	103		
3-*tert*-butylcyclohexenone	AN	156	103	(5.1×10^8)
phenanthrone (**8**)	AN	131		
	IPA	150	145	4.0×10^8
cyclopentenone (**4**)	AN	380[g]	47[h]	(4.1×10^9)
	CH	185[g]	80[i]	(1.3×10^{10})
testosterone acetate (**6b**)	AN	385	413	(4.4×10^9)
	AN	380	295	5.0×10^9
	CH	292		
testosterone (**6a**)	AN	330		
	CH	440[e]		
$\Delta^{1,6}$-bicyclo[4.3.0]nonen-2-one (BNEN, **9a**)	AN	1460	nd[j]	$>10^{10}$[j]
	CH	1860		
5,5-diMeBNEN (**9b**)	IPA	1400	1500	4.5×10^9
	t-BuOH	2300		
3-phenylcyclohexenone	AN	2760		(2×10^6)

[a] Key: CH, cyclohexane; AN, acetonitrile: IPA, isopropyl alcohol. [b] Values directly determined from decay of transient absorption; estimated error 10%. [c] Values in parenthesis determined independently by R. A. Caldwell and W. Tang, University of Texas at Dallas, private communication. [d] Value determined from extrapolation to zero quencher concentration of data for rates of triplet energy transfer to NA (MN); see text. [e] Reference 4. [f] Since the Stern–Volmer plot in this case had a low correlation coefficient, the derived parameters are considered to have a larger than usual associated error. [g] Lifetime data extrapolated to infinite dilution, according to eq 2. [h] At 0.06 M CP, for which a value of 43 ns for the triplet lifetime is calculated from eq 2. [i] At 0.016 M CP for which a lifetime of 67 ns is calculated from eq 2.

Soon afterward, Bonneau reported the results of TAS studies on methyl vinyl ketone (**2**), cycloheptenone (**3**), cyclopentenone (CP, **4**) cyclohexenone (CH, **5**), and testosterone (TE, **6a**).[4] In each case, excitation at either 265 or 353 nm resulted in short-lived transient absorption in the 260–280-nm region, which decayed with first-order kinetics. This transient absorption was fully developed within the rise time of the laser pulse (5 ns), except for testosterone where the transient absorption developed over ca. 20 ns. In these initial studies, the transient lifetimes measured for compounds **2**–**6a** in cyclohexane solution were 8, 11, 25, 30, and 440 ns (Table I). In all cases, the addition of oxygen led to enhanced decay rates. Addition of piperylene (1,3-pentadiene) caused an increase in the rate of decay of transient absorption in the cases of **4**, **5**, and **6a**. From these data and their resemblance to the earlier findings on acetylcyclohexene (**1**),[3] it was concluded that these transient species are orthogonal or twisted triplet states of the enones, in which the angle of twist around the C=C bond varies with the conformational rigidity of the enone chromophore.[4] It was proposed that in cases (**1**, **2**, and **3**) where twisting in the ground state by 90° or more is structurally feasible, the orthogonal triplet state should be readily accessible and would have a short lifetime because of strong coupling with the ground state at the perpendicular configuration. Structural constraints to twisting would be expected to increase the lifetime of the enone triplet, as observed in the cases of **4**, **5**, and particularly **6a**.

In the case of CP (**4**), in addition to what was concluded to be a monomeric triplet with a lifetime of 30 ns, Bonneau observed a second slightly longer lived (ca. 40 ns) transient showing absorption in the 360–400-nm region, which was suggested to be a triplet excimer or a triplet 1,4-biradical en route to CP photodimers, on the basis of coincidence of kinetic parameters with those measured by Wagner and Bucheck in steady-state experiments.[5] However, it was concluded that this dimeric species was *not* derived from the 280-nm transient, (i.e., the monomeric enone triplet) since the optical density of the 365-nm transient was strongly decreased upon addition of piperylene, which had little if any effect on the lifetime of the 280-nm transient.[4] As will be discussed below, these anomalies have been resolved in recent flash kinetic studies of CP.[6]

For cycloheptenone (**3**), an additional long-lived transient absorbing at 265 nm has properties (enhanced rate of decay in protic vis a vis nonpolar solvents and lifetime dependence on solvent acidity) that are consistent with those expected for ground-state *trans*-cycloheptenone.[8] This species decays by mixed second- and first-order kinetics, corresponding to dimerization and isomerization to the more stable cis isomer, respectively.

The direct observation of twisted triplet excited states of cyclic enones[3,4,7] was of particular interest because of the earlier suggestion[9] that the lumiketone photorearrangement of 4,4-disubstituted cyclohexenones to bicyclo[3.1.0]hexan-2-ones proceeds via twisted enone triplet states. Though it has a low quantum efficiency, this rearrangement is stereospecific and does not proceed via triplet biradicals that are capable of undergoing stereomutation at C_4. This observation puts severe constraints on the geometry

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of the reactive enone triplet as well as on the transition state for the photoisomerization.[9] Twisted cyclohexenone triplets have also been invoked to rationalize the formation of trans-fused bicyclo[4.2.0]octan-2-ones upon [2 + 2] photocycloaddition of alkenes.[10]

Lifetimes and energies of the triplet states directly involved in photoreactions of cyclic enones, and rate constants for the various radiationless decay processes of these triplets (including product formation), are of fundamental importance in discussions of structure–reactivity relationships in enone photochemistry. Previously, such information could be obtained only indirectly from the quantum yields of phototransformations and the efficiencies of their quenching by standard triplet quenchers, on the basis of assumed rate constants for energy transfer from the reactive enone triplet to the quencher (usually naphthalene or a conjugated diene).[5,9] The possibility of directly measuring lifetimes of reactive triplets of cyclic enones precludes the necessity of such assumptions and allows discussions of photochemical reactivity in these systems to be put on a much firmer foundation. This paper contains detailed accounts of our studies carried out over the past 10 years, portions of which have been reported previously only in preliminary form.[11,12]

Experimental Section

Synthesis of Enones and Sample Preparation. Cyclopentenone, cyclohexenone, 3-methylcyclohexenone, 4,4-dimethylcyclohexenone, testosterone, and testosterone acetate were obtained commercially. The remaining enones were prepared and characterized by known methods. All enone samples were purified by the appropriate combination of distillation, recrystallization, column chromatography, and preparative GLC. Details are available in refs 13–15. Spectrograde solvents, obtained commercially, were used throughout. Sample solutions for flash photolysis studies were prepared by weighing the enone into a quartz cuvette (path length 0.1–2 cm, usually 1.0 cm), followed by the addition of the quantity of solvent (usually 2.0 mL) required for adjustment of the optical density between 0.3 and 1.5 at the excitation wavelength (usually 355 nm). The solutions were purged with nitrogen or argon for at least 5 min, prior to the experiment.

Apparatus and Procedures. The nanosecond laser flash photolysis setups used in Bordeaux, in Ottawa, and at Columbia University are very similar but differ in details such as the type of laser used or in the arrangement of the exciting and analyzing beams.

In Bordeaux,[4,16] a mode-locked Quantel Nd-YAG laser was used, providing, after pulse selection, amplification, and frequency conversion, single pulses of duration of ca. 200 ps and energies of tens of millijoules, at 353 or 265 nm.

In Ottawa,[17] a Molectron UV-24 nitrogen laser, providing pulses of ca. 8 ns and energies >20 mJ at 337 nm, was used. In a few experiments, a Lumonics TE-860-2 XeCl excimer laser, providing pulses of duration of ca. 5 ns (20 mJ/pulse) at 308 nm, was employed.

In experiments carried out at Columbia University, a Quanta Ray Q-switched Nd-YAG laser was used. After pulse selection, amplification, and frequency conversion, it provided pulses of duration of ca. 6 ns and energies of 2–5 mJ, at 355 nm.

In all three systems, the analyzing light was provided by a pulsed, high-pressure mercury or xenon arc. In most cases, the exciting and analyzing beams were oriented at right angles (crossed-beam arrangement). The enone concentration was usually in the range 0.01–0.05 M (OD 0.3–0.7 at the wavelength of excitation) but was somewhat higher (OD 1–1.5) in Bordeaux,[16] where a crossed-beam arrangement with an angle of 45° was used for a few concentrated (OD >1.5) samples. In Ottawa, a crossed-beam arrangement with an angle of 30° was used throughout. Transient UV–vis absorption spectra were obtained either by recording the transient signal at successively increasing analyzing wavelengths (Bordeaux and Ottawa) or with the aid of a multichannel spectrum analyzer (Columbia University).

For kinetic experiments, the analyzing beam was passed through the sample cell and then through a monochromator onto a RCA IP-28 photomultiplier. The photomultiplier response was fed to a Tektronix 7912-AD digitizer and the digitized signal analyzed by computer, with use of basically similar, dedicated software developed separately in each laboratory. In Bordeaux, transient decay curves deriving from a single laser pulse were analyzed separately and the results of several measurements averaged to give the data reported in Table I. For most compounds, the measurements were repeated with several independently prepared solutions of the enone in a given solvent. In Ottawa and at Columbia University, the data from 5–30 laser pulses (depending on the signal to noise ratio) were averaged, prior to computer processing. The measurements in these laboratories included a background correction, involving substraction of the photomultiplier response recorded with the analyzing beam blocked from the transient absorption signal.

Quenching experiments were performed with outgassed enone solutions having optical densities ranging from 0.3 to 0.7 (at 355 nm in 1-cm quartz cells). Aliquots of either the neat or the dissolved quencher were added by using a microliter syringe. Depending on the signal to noise ratio, data from 5–20 laser pulses were averaged in each kinetic experiment. In studying the quenching of enone triplets by oxygen, triplet lifetimes were measured at increasing oxygen concentrations, corresponding to purging the solution with nitrogen ($[O_2] = 0$), air ($[O_2] = 0.0021$ M), a 1:1 nitrogen–oxygen mixture ($[O_2] = 0.005$ M), and pure oxygen ($[O_2] = 0.01$ M), respectively.[18]

Although the data collection and analysis were computer controlled at all three laboratories, there are a number of subjective decisions that may affect the quality of the results. Firstly, the region of the transient decay or growth curve to be analyzed is manually selected: The points at the tail and (in the case of a decay curve) at the very beginning of the curve have the highest error and, therefore, are usually discarded. Secondly, for decay curves, the base line corresponding to zero transient absorption and the asymptote corresponding to complete exponential decay are also manually selected: In some cases, the decay curve returns to the base line, but in several situations long-lived residual absorption due to unidentified intermediates or photolysis products persists. From a third line, corresponding to transient absorption of all the analyzing light, the optical density of the transient is computed as a function of time and the data is then fit to either mono- or biexponential first-order kinetics or to other kinetic models. Small inconsistencies in the manual selection of the base line corresponding to zero transient absorption as well as the asymptote of the experimental decay curve can cause a significant spread in the calculated transient lifetimes, without affecting the correlation coefficient (i.e., the quality) of the fit to first-order decay kinetics. In most runs, the fit between experimental and calculated decay curves was excellent ($r > 0.98$) and no systematic error was observed in plots of residuals. Runs were discarded for which either the correlation coefficient of the fit between the experimental and calculated decay curves was below 0.98 or in which a systematic error in the plot of the residuals was noticeable. From the variations in the triplet lifetimes evaluated from different runs on the same enone sample, the error in the triplet lifetimes, evaluated by the present subjective, interactive method of analyzing the data, is estimated to be about ±10%.

Similar problems were encountered in analyzing the experimental data concerning the kinetics of growth of the naphthalene (NA) or 1-methylnaphthalene (MN) T_1–T_n transient (at 413 and 420 nm, respectively) generated via energy transfer from the enone triplet. In this case, the present, interactive data analysis method requires the manual selection of an asymptote corresponding to the limiting OD of the acceptor triplet absorption. However, since the actual experimental trace is a

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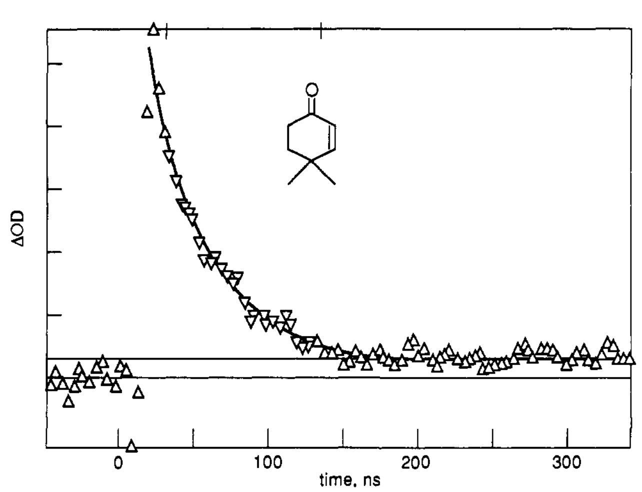


Figure 1. Decay of transient absorption at 280 nm from excitation of 4,4-dimethylcyclohexenone in acetonitrile at room temperature with a nitrogen laser at 337 nm. Data points are the average of 20 laser shots.

composite of transient growth and subsequent decay, this asymptote does not coincide with the point of maximum transient absorption. Slight inconsistencies in the manual selection of this asymptote were found to introduce a large spread in the calculated first-order rate constants for the growth of the quencher's triplet absorption. An approach used in later experiments involved a more accurate measurement of the monoexponential decay portion of the experimental trace, by adjustment of both the time base and delay of the digitizer. By subsequent extrapolation of this trace to $t = 0$ (the moment of laser excitation), the limiting OD value for the transient absorption of the quencher triplet was determined. An alternative approach, utilized in a few experiments, was to fit the experimental transient absorption curve to a biexponential kinetic model involving successive first-order growth and decay processes, the latter being determined from the tail of the experimental trace. Insofar as the quality of the results is concerned, neither approach gave an advantage over the simpler method of fitting appropriate sections of the experimental trace to monoexponential first-order growth or decay kinetics.

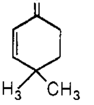
Results

Enone Triplet Lifetimes. Table I summarizes all the kinetic data obtained in the present study and relevant data from the literature.[4,6] The quantity τ_{dir} (column 3) gives the enone triplet lifetimes measured directly from the decay of the transient absorption at or near 280 nm upon excitation at 266, 308, or 353 nm (see Experimental Section for details). Except as discussed below, the decay of transient absorption under these conditions followed clean first-order kinetics. The values labeled τ_{exl} (column 4) are derived from kinetic studies of triplet energy transfer from the enones to NA or MN. Following the laser pulse, the growth of NA or MN triplet absorption was monitored at 413 and 420 nm, respectively. The growth rates are given by eq 1, where τ_{obs}

$$k_{obs} = (\tau_{obs})^{-1} = (\tau_0)^{-1} + k_q[Q] \qquad (1)$$

is the rise time for appearance of NA (or MN) triplet absorption at 413 (or 420 nm), τ_0 ($=\tau_{exl}$) is the lifetime of the donor (enone) triplet in the absence of quencher, and k_q is the second-order rate constant for quenching by triplet energy transfer. Values of k_q and τ_0 were derived from the slope and intercept, respectively, of plots of k_{obs} vs the quencher concentration. Problems associated with accurate determination of k_{obs} have been discussed in the Experimental Section. In addition, errors in τ_{exl} deriving from extrapolation of the quenching data to zero quencher concentration may be particularly large in the case of longer lived enone triplets, where values of $1/\tau_0$ are small. For the most part, there is excellent agreement between the values of the enone triplet lifetimes obtained by the two techniques, demonstrating that the species being quenched by NA and MN is indeed the transient showing $T_1 \rightarrow T_n$ absorption in the 260–300 nm region. Furthermore, agreement between values of $k_q\tau_T$ obtained from the flash data and Stern–Volmer slopes for quenching by NA and MN of photorearrangement of a number of these cyclohexenones[2,11a,19,20] indicates that the cyclohexenone triplets absorbing at 260–310 nm are intermediates in photochemical transformations of these enones.

In several cases, the enone transient absorption in the 280–400-nm region does not decay to the zero-absorption base line. This is evident for 4,4-dimethylcyclohexenone (DiMeCH, **7**) in acetonitrile (Figure 1), where the residual optical density at 280 nm is ca. 5–10% of the maximum OD generated in the flash. On the digitizer time base utilized for measuring the triplet decay in this system (200 ns full scale), the residual absorption decays very slowly if at all; in the kinetic analysis, it is taken as the limiting OD of the transient decay. No attempts were made to analyze this decay with longer time bases. A similar residual OD was observed for cyclohexenone but was reduced to <5% of the maximum transient OD for the 2-methyl, 3-methyl, 3-ethyl and 3-*tert*-butyl analogues. In the case of phenanthrone (**8**), on the other hand, the residual OD was negligible. Speculation on the possible origin of this residual absorption is reserved for the Discussion.



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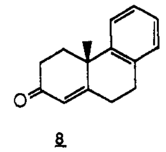

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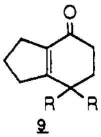

9
a, R=H
b, R=CH3

Effect of Enone Concentration on Triplet Lifetimes. Self-Quenching. (a) Cyclopentenone. Bonneau reported[4] that the triplet lifetime of 30 ns measured for CP in deaerated cyclohexane was "nearly unaffected" by increasing the enone concentration from 0.1 to 1.0 M. However, in recently published studies done in collaboration with Caldwell,[6] the effect of the CP concentration on the CP triplet lifetimes in cyclohexane and acetonitrile in accord with the self-quenching relationship shown in eq 2 (E = CP) was

$$(\tau_{obs})^{-1} = k_d + k_{sq}[E] \qquad (2)$$

observed. The reciprocals of the intercepts of plots of $1/\tau$ vs [CP] give CP triplet lifetimes at infinite dilution (τ_0) in acetonitrile and cyclohexane of 380 and 185 ns, respectively.[6] The rate constants for self-quenching, k_{sq}, were 2.7×10^8 and 5.9×10^8 M^{-1} s^{-1}, respectively.[6] In earlier studies, Wagner[5] reported that $\tau_0 = 25$ ns and $k_{sq} = 6.6 \times 10^8$ M^{-1} s^{-1} for CP in acetonitrile from quenching of CP photodimerization by piperylene. A diffusion-controlled rate constant for triplet energy transfer from CP to piperylene of 1.0×10^{10} M^{-1} s^{-1} was assumed, which is much larger than values of k_q for quenching by dienes of CP and other enone triplets determined in the present study (see below). In order to resolve the discrepancy between the CP triplet lifetime of 30 ns determined by Bonneau[4] with the significantly longer lifetimes determined recently,[6] we propose that the species observed in the earlier studies (carried out at relatively high CP concentrations) was not the monomer triplet but the dimeric triplet 1,4-biradical, which absorbs in the same spectral region.[6] This would also explain a number of otherwise anomalous experimental observations[4] concerning CP alluded to earlier. Kelly[21] reports that k_{sq} for 3-phenylcyclopentenone is 2.5×10^8 M^{-1} s^{-1}, a value similar to that found for CP.[6]

(b) Cyclohexenones. Monocyclic Systems. A study of the effect of varying enone concentration on the triplet lifetimes of CH and diMeCH (**4** and **8**) in spectrograde hexane was made at the Regional Laser Laboratory at the University of Pennsylvania. (See ref 15 for details). Assuming an error of ca. 10% in the triplet lifetimes, no variation in either the transient lifetime or the transient absorbance at 265 nm was observed in the concentration range 0.31–1.20 M for CH and 0.32–0.99 M for 4,4-diMeCH. The triplet lifetime of 3-MeCH in acetonitrile also did not vary

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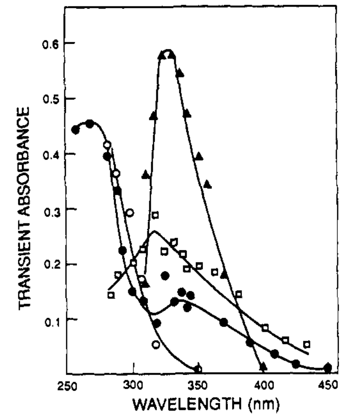


Figure 2. Absorption spectra of transients derived from 4,4-dimethylcyclohexenone in acetonitrile (●), phenanthrone (**8**) in acetonitrile (○), BNEN **9b** in ethanol (□) and steroid dienone **12** in ethanol (▲). Excitation at 353 nm except for **8** where excitation was at 266 nm.

systematically when the enone concentration was increased from 0.009 M (τ = 70 ns) to 0.095 M (τ = 76 ns). In this system, the transient decay rate was also independent of the analyzing wavelength (300, 345, 370, and 400 nm) at a fixed enone concentration (0.035 M).

Testosterone Acetate. For longer lived structurally constrained triplets containing a cyclohexenone moiety, the decay kinetics were more complicated. Thus, for testosterone acetate (TA, **6b**) in cyclohexane (excitation at 355 nm, OD_{355} 0.6), substantial residual long-lived absorption occurs between 270 and 350 nm, being particularly prominent at the shorter wavelengths. The absorption decay data could be fit by using a kinetic model involving two consecutive first-order decays, with lifetimes of ca. 300 ns and 9 μs, respectively. Similar consecutive exponential decays were observed for TA in 2-propanol (excitation at 266 nm, OD_{266} 1.1, detection at 310 nm), with lifetimes of ca. 400 and 2.9 μs. Interestingly, the long-lived component was not evident in experiments carried out in aerated or oxygenated solutions. The optical density but not the lifetime of the long-lived component was found to increase as a function of TA concentration. Simulations based on a biexponential kinetic decay model indicated that the initial component had a lifetime that decreased with increasing TA concentration, while the lifetime of the second component varied between 3 and 6 μs but showed no clear trend as a function of TA concentration. These observations clearly suggest that self-quenching of TA triplets is a significant process, with $k_{sq} \approx 6 \times 10^6$ M^{-1} s^{-1} in acetonitrile; thus, the limiting triplet lifetimes for TA in very dilute solutions are presumably slightly longer than indicated in Table I.

Bicyclo[4.3.0]nonenone (BNEN) (9a). For this enone, two long-lived transient decays were observed at all concentrations studied. The second transient displays a higher absorption at shorter wavelengths (285–305 nm). In aerated solutions, a long tail on a relatively rapid first-order decay curve (97 ns) is visible. The rate of the initial portion of the transient decay curve monitored at 285 nm was assigned to the monomeric triplet. Its contribution to the transient OD decreases at higher BNEN concentrations in acetonitrile. The data fit self-quenching kinetics (eq 2) with k_{sq} (2.6 ± 0.4) × 10^7 M^{-1} s^{-1} and an extrapolated triplet lifetime at infinite dilution of 1.6 ± 0.2 μs.

Table II. Rate Constants for Quenching of Enone Triplets by Oxygen

enone	E_T, kcal/mol	solvent[a]	k_q, 10^9 M^{-1} s^{-1}	ref
BNEN (**9a**)	73.8	AN	4.6	*b*
4,4-diMeBNEN (**9b**)	*c*	EtOH	4.2	*b*
		CH	2.5	*b*
testosterone (**6a**)		EtOH	2.2	4
testosterone acetate (**6b**)	70.3	AN	3.0	*b*
		EtOH	2.2	*b*
dehydrotestosterone (**12**)	*c*	EtOH	1.7	11d
octalone (**10**)	*c*	AN	4.5	*b*
phenanthrone (**8**)	*c*	AN	7.1	*b*
		IPA	2.5	*b*
cyclopentenone	(70)[d]	AN	4.7	*b*
		CH	5	4
3-MeCH	68.7	AN	5.3	*b*
3-tBuCH	70.1	AN	2.9	*b*
3-EtCH	66.9	AN	2.9	*b*
2-MeCH	66.7	AN	2.4	*b*
cyclohexenone	62.7	CH	5.6	4, *b*
4,4-diMeCH (**7**)	63.3	AN	7.1	*b*
		CH	7.5	*b*
		EtOH	5	*b*
3-PhCH	54.7	AN	2.1	*b*
		CH	2.7	43
acetylcyclohexene (**1**)	*c*	CH	3.5	4

[a] AN = acetonitrile, CH = cyclohexane, IPA = isopropyl alcohol, EtOH = ethanol. [b] This work. [c] Not determined. [d] Approximate value (see text).

Triplet Absorption Spectra. All of the enones studied show transient absorption extending from ca. 250 to 400 nm. Transient absorption below 250 nm could not be studied because of the strong absorption by enone ground states in this spectral region as well as instrumental limitations. Bonneau reported[4] that the maximum in the absorption spectum of the "twisted" cyclohexenone triplet was at 260–280 nm and was shifted to 310 nm in the case of testosterone (**6a**).[4] With use of benzophenone as reference, it was determined that ϵ_{270} for both cyclohexenone and cyclopentenone triplets is >2 × 10^3 M^{-1} cm^{-1}.[4]

Ultraviolet absorption spectra of the enone triplets of **6a**, **7**, **8**, and **9** shown in Figure 2 were derived from point by point measurements of the initial OD at 10-nm intervals between 260 and 450 nm as produced by a single excitation pulse, corrected for variations in the pulse energy. For 4,4-diMeCH (**7**), the transient absorbance was determined by two methods, i.e., the standard crossed-beam arrangement at wavelengths (280–300 and 370–450 nm) where ground-state absorption is low, and a quasi-colinear arrangement at probe wavelengths where ground-state absorption is appreciable, utilizing lower enone concentrations. Measurements using the two methods were normalized by comparison of the transient absorbance measured at 290 nm by both methods. The laser excitation wavelength was 355 nm for **6a**, **7**, and **9** and 266 nm for **8**. Excitation of phenanthrone (**8**) at 355 nm gave rise to an additional transient absorption centered at ca. 420 nm, attributed to a trace impurity in the enone sample.[22] Figure 3

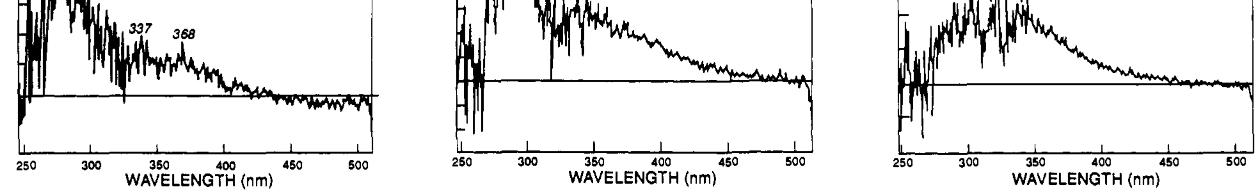
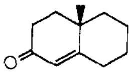


Figure 3. Triplet absorption spectra produced by 353-nm excitation of 0.01 M solutions in acetonitrile of (a) octalone (**10**), (b) testosterone acetate (**6b**) and (c) BNEN (**9a**). Spectra were obtained at Columbia from single laser pulses by using a multichannel analyzer.

shows the triplet absorption spectra recorded at Columbia by 353-nm excitation of 10^{-2} M solutions of octalone (**10**) and enones **6b** and **9** by using a multichannel analyzer.



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Quenching of Enone Triplets. (a) Oxygen. Table II contains rate constants for quenching of enone triplets by oxygen, measured by the change in the transient lifetimes monitored at or near 280 nm as a function of O_2 concentration. Bonneau's earlier data[4] on enones **1**, **4**, **5**, and **6a** are also included. Oxygen concentrations were not directly measured but were calculated from tables of oxygen solubilities in organic solvents.[18] Details of procedures are given in the Experimental Section. Stern–Volmer plots of transient decay rates vs oxygen concentration were linear in all cases. In all cases, k_q is $>10^9$ M^{-1} s^{-1}, but variations in k_q between conformationally rigid and flexible enone chromophores are seen that are similar in magnitude and direction to those seen with arylalkene and other triplets.[23,24] Such variations have traditionally been interpreted in terms of changes in mechanisms for oxygen quenching.[23,24] However, thus far we do not find any correlation between k_q values and singlet oxygen quantum yields.[25]

(b) Aromatic Hydrocarbons. Because of the strong ground-state absorption by naphthalene (NA, E_T 60.9 kcal/mol)[18] and 1-methylnaphthalene (MN, E_T 59.6 kcal/mol)[18] in the 260–300-nm region, the rate constants for triplet energy transfer (Table I) were determined from the growth rates of the NA and MN triplet absorption at ca. 420 nm (see eq 1). Quenching of 4,4-diMeCH triplets by acenaphthene (E_T 59.2 kcal/mol)[18] in cyclohexane, studied by monitoring the enone triplet decay at 280 nm, gave a linear Stern–Volmer plot with a slope (k_q) of 4.2×10^8 M^{-1} and an intercept corresponding to $\tau_0 = 26$ ns. Neither biphenyl (E_T 65.8 kcal/mol)[18] nor phenanthrene (E_T 62 kcal/mol)[18] quenched 4,4-diMeCH triplets, suggesting triplet energy transfer is endothermic in these cases.

The rate constants for triplet energy transfer from CH and diMeCH to MN in cyclohexane as well as the MN triplet lifetime (ca. 4.5 μs) were found to be independent of the enone concentration. No systematic variation in the rate of triplet energy transfer to NA (0.01 M) upon excitation at 353 nm was detected when the concentration of 4,4-diMeCH was varied between 0.048 and 0.52 M in acetonitrile; the value of τ_{growth} was 18 ± 2 ns at the six different enone concentrations examined. This is consistent with the absence of an enone concentration effect on the triplet decay rates at 280 nm (see above). These results further demonstrate that triplet energy transfer from these enones to MN is irreversible, indicating that the triplet energies of CH and 4,4-diMeCH are at least 3 kcal/mol greater than that of MN.

In the case of BNEN (**9a**), for which two transient decays were observed in the 275–400-nm region (see above), the growth of NA triplet absorption at 413 nm was cleanly monoexponential, indicating that only one of the two components observed by transient absorption is transferring triplet energy to naphthalene. The rise time of $^3NA^*$ absorption is 200 ns at 5×10^{-4} M NA, corresponding to a rate constant of 8.5×10^9 M^{-1} s^{-1} for quenching of the shorter lived (1.6 μs) component. A rate constant exceeding k_{diff} would be required if the second component were being quenched by naphthalene.

(c) Nitroxyl Radicals. Stern–Volmer plots for quenching by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) of triplets derived from phenanthrone (**8**) in acetonitrile and bicyclononenone **9b** in ethanol were approximately linear, with slopes (k_q) of (2.4 ± 1.7) × 10^8 and (3.5 ± 1.1) × 10^8 M^{-1} and intercepts corresponding to τ_0 of 184 ns and ca. 6 μs, respectively (the latter kinetic parameter is particularly imprecise because of the required extrapolation). Similar Stern–Volmer plots for quenching of 4,4-diMeCH triplets by both TEMPO and its 4-hydroxy derivative display pronounced downward curvature at nitroxyl concentrations above 0.3 M, presumably because of self-association of the nitroxyl radicals.[26] Quenching rate constants of ca. 10^9 M^{-1} were estimated from the initial slopes.

Table III. Rate Constants for Quenching of Enone Triplets by Piperylene and 2,5-Dimethyl-2,4-hexadiene (DMCH)

enone	k_q, M^{-1} s^{-1}	plot character
	Quenching by Piperylene	
3[a]	inefficient	
CP (**4**)[a]	$<10^8$	
CH (**5**)[a]	4×10^7	curved
6a[a]	ca. 10^9	straight line
7	$<10^8$	curved
8	2.2×10^8	roughly linear
9a	ca. 10^9	straight line
	Quenching by DMCH	
CP	1.11×10^9	curved
3-MeCH	1.28×10^8	straight line
2-MeCH	4.00×10^7	curved
3-*t*-BuCH	2.44×10^8	curved
3-PhCH	1.82×10^9	straight line

[a] Reference 4.

(d) Dienes. Quenching of enone triplets by conjugated dienes continues to give anomalous results. Bonneau reported[4] that addition of piperylene strongly decreases both the optical density and the lifetime of the triplet derived from testosterone (k_q ca. 10^9 M^{-1} s^{-1}), while piperylene "hardly" affected the lifetimes of the transients produced from CP (**4**) and CH (**5**). In the present study, quenching of CH and diMeCH triplets by piperylene in aerated cyclohexane resulted in Stern–Volmer plots that show downward curvature at diene concentrations above ca. 0.2 M. On the other hand, quenching of triplets of 4,4-diMeCH (**7**) by up to 0.6 M piperylene gave a linear Stern–Volmer plot with k_q = (4.5 ± 0.5) × 10^7 M^{-1} s^{-1}, i.e., 2 orders of magnitude below the diffusion-controlled rate.

The results of quenching studies using 2,5-dimethyl-2,4-hexadiene (DMCH) (E_T 57.2 kcal/mol)[27] as the quencher are summarized in Table III. For 0.023 M CP in acetonitrile, a linear Stern–Volmer plot was obtained for diene concentrations up to 0.02 M, with $k_q = 1.11 \times 10^9$ M^{-1} s^{-1} and $\tau_0 = 64$ ns; the latter is in accord with the CP triplet lifetime at this concentration measured independently by kinetic absorption spectroscopy (KAS) at 280 nm.[6] A similar study with 3-methylcyclohexenone (3-MCH, **10**) in acetonitrile gave $k_q = 1.3 \times 10^8$ M^{-1} s^{-1} and an extrapolated enone triplet lifetime of 74 ns, in excellent agreement with the value for τ_0 given in Table I.

(e) Alkenes and Amines. Results of studies of interactions of enone triplets with alkenes, which bear directly on the mechanism of [2+2] photocycloadditions, are discussed elsewhere.[11e,15,19,28] TAS and product studies have conclusively demonstrated that amines directly quench monomeric enone triplet states, not triplet excimers,[29,30] leading to a variety of products.[11b,15,19,31,32] Details of these investigations can be found in the cited references.

Picosecond Flash Studies. These studies were conducted (at the Laser Laboratory at the University of Pennsylvania) to determine the rise time of the transient absorption at 280 nm attributed to enone triplets. The picosecond flash system[33] was

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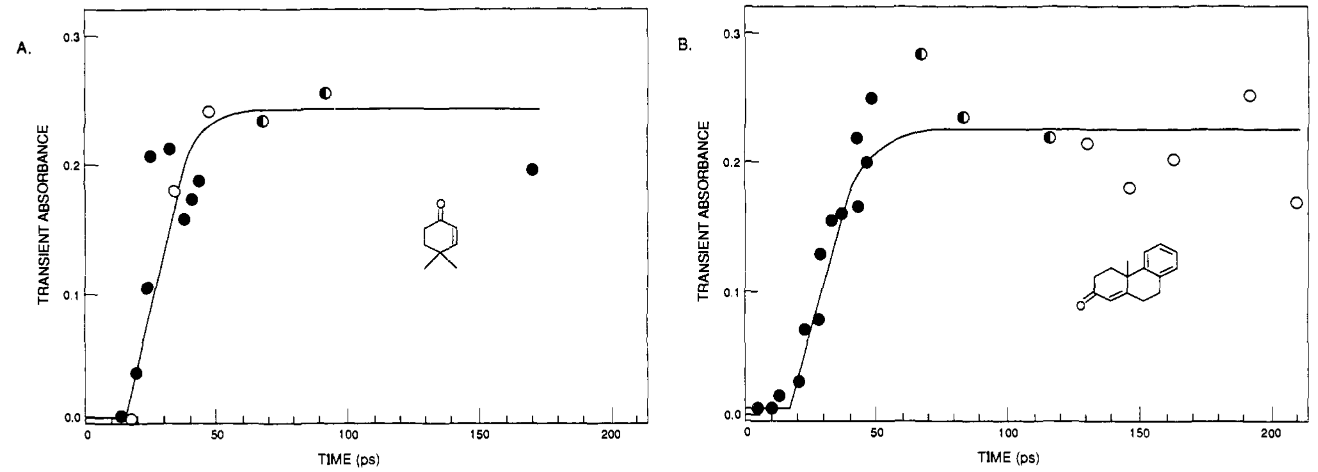


Figure 4. Growth of transient absorption from picosecond flash excitation at 353 nm of solutions of (a) 4,4-dimethylcyclohexenone in 2-propanol and (b) phenanthrone (**8**) in acetonitrile. Open and closed circles in each case are data from separate runs, and each point is the average of 10 measurements. Half-closed circles represent the average of open and closed circles at that particular delay time.

modified slightly for these experiments. Solutions of 4,4-diMeCH (**7**) in isopropyl alcohol and phenanthrone (**8**) in acetonitrile (optical densities 0.2–0.5 at 353 nm) were excited with 20-ps laser pulses at 353 nm, generated by frequency tripling of the output from a Nd:YAG laser, and the transient absorption was measured at varying delay times. Figure 4 shows the development of transient absorption for **7** and **8** at 280 nm from 0 to 200 ps following excitation. It is clear that transient absorption for **7** and **8** at 280–285 nm is generated very rapidly. A rough estimate of the growth rate in both cases is 15–30 ps, which is comparable to the width (20 ps) of the laser pulse.

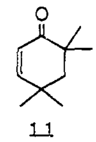
These results indicate that the transients derived from **7** and **8** showing absorption at 280 nm, proposed to be relaxed T_1 π,π^* states (see Discussion), are generated within 20 ps by either intersystem crossing from a singlet state or rapid internal conversion from an upper triplet state. It is not possible to distinguish between these possibilities at this time.

Discussion

Origin of Transient Absorption at 280–350 nm on Laser Flash Excitation of Cyclic Enones. As shown below, our results strengthen the original proposal of Bonneau[4] that the enone transients observed at 280–350 nm with lifetimes in the nanosecond regime are twisted excited π,π^* triplet states.

It was suggested by Pienta[30] that the transient absorption in the 280-nm region is due to a triplet excimer, not to a monomeric triplet species. This suggestion is not in accord with the observation that the optical density of the transient in several instances is independent of the enone concentration (4,4-diMeCH was studied most extensively in this regard). Moreover, for CP, TA, and BNEN, the transient lifetime decreases with increasing enone concentration, consistent with consumption of the triplet and formation of some sort of dimeric intermediate, en route to enone photodimers. In recent studies on CP,[6] a dimeric triplet 1,4-biradical with a lifetime of 37 ns was detected. In the cases of CP, 3-MCH, TA, and BNEN, the 280-nm transient is quenched by alkenes concomitant with formation of 1:1 enone–alkene [2 + 2] cycloadducts; it is considered to be highly unlikely that simple alkenes are intercepting triplet excimers and not monomeric enone triplets. It is known, for example, that monomeric enone triplets and not triplet excimers are the species quenched by amines by an electron transfer mechanism.[31,32]

An alternative possibility is that the 280-nm transient might be a triplet state of the enol tautomer of the enone. For cyclohexenone, this would correspond to triplet 2-hydroxy-1,3-cyclohexadiene. This assignment is plausible, since 1,3-cyclohexadiene triplets are known to absorb at ca. 280 nm.[34] However, this possibility is ruled out by the finding that flash excitation of 4,4,6,6-tetramethylcyclohex-2-en-1-one (**11**), which is structurally incapable of enolization, produced a transient displaying a spectrum and lifetime similar to those of cyclohexenone and its 4,4-dimethyl analogue.



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Typical triplet quenchers reduce the lifetimes of the observed transients, providing additional support for their assignment as enone triplets. In the case of oxygen, small variations in the quenching rate constants are observed as a function of enone structure, similar to those seen in studies of arylalkene triplets;[23,24] the significance of these variations has yet to be established.[25] Other triplet quenchers, such as dienes and nitroxyl radicals, also quench the observed transients, although the Stern–Volmer plots frequently show pronounced curvature (see later discussion). Nanosecond flash excitation of the cyclic enones in the presence of naphthalene (NA) or 1-methylnaphthalene (MN) leads to formation of NA and MN triplets, which absorb at ca. 420 nm. The rates of triplet energy transfer, determined from the rise time of triplet NA or MN absorption, varied linearly with the quencher concentration, resulting in linear Stern–Volmer plots (eq 1). The donor (enone) triplet lifetimes in the absence of quencher (τ_{exl}) derived from these plots are in excellent agreement with the triplet lifetimes (τ_{dir}) derived from decay of transient absorption in the 280–350 nm region. The product of k_q and τ_T from the present studys agrees well with $k_q\tau_T$ determined from steady-state quenching by NA and MN of photoreactions of theses enones.[11a,19,20,35] Thus, it can be concluded that the triplets observed in these kinetic studies are indeed intermediates in these photoreactions. The variation of the quenching rate constants as a function of enone structure and triplet energy will be discussed below.

Transient Absorption Spectra. The transient absorption spectra for enones determined in this study are similar to those previously reported.[4] All compounds display a relatively broad $T_1 \rightarrow T_n$ absorption in the 250–400 nm region with λ_{max} 280–320 nm. 4,4-Dimethylcyclohexenone (**7**) shows two maxima, at 268 and 345 nm. For this and several other enones, the rate of decay of transient absorption was found to be independent of the monitoring wavelength. Transient spectra of enones with more rigid structures, such as **6** and **9**, were red-shifted and broadened relative

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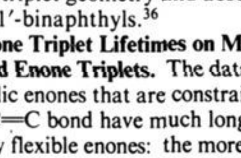
to those of conformationally flexible enone triplets.

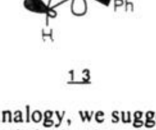
A similar difference between UV spectra of planar and twisted triplet states of a series of α-naphthylethylenes and related styrene derivatives has been reported.[23] The red-shift of the $T_1 \rightarrow T_n$ absorption is greater the more coplanar the aromatic system is with the exocyclic C=C bond. Deviation from planarity in these styrenes is due primarily to steric crowding between substituents on the aromatic and ethylenic moieties; coplanarity was enforced by incorporating these moieties into relatively rigid fused ring systems. The similarity in the findings in the present study and the results of the α-naphthylethylene study[23] is striking. A similar relationship between triplet geometry and absorption spectra has been reported for 1,1′-binaphthyls.[36]

Dependence of Enone Triplet Lifetimes on Molecular Structure. Geometries of Relaxed Enone Triplets. The data in Table I clearly demonstrate that cyclic enones that are constrained in their ability to twist around the C=C bond have much longer triplet lifetimes than conformationally flexible enones: the more flexible the enone, the shorter the lifetime. Thus, the triplet lifetimes of the simple cyclic enones of ring size *n* increase in the order $n = 7 < 6 < 5$, while the lifetime of triplets of phenanthrone (**8**) is intermediate between those of the 4,4-dimethylcyclohexenone (**7**) and testosterone (**6a**). Incorporating an additional olefinic bond in linear conjugation with the enone moiety as in **12** has been shown[11c] to result in a dramatic increase in the triplet lifetime. A similar increase observed for 3-PhCH will be discussed later.

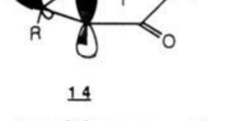


12

These data can be rationalized according to Bonneau's model[4] in which twisting around the C=C bond causes an increase in energy along the ground-state potential energy surface (S_0) and a concomitant decrease in energy along the T_1 $^3(\pi,\pi^*)$ surface.[37] This minimizes the T_1–S_0 gap and facilitates T_1–S_0 radiationless decay in a process presumably dominated by spin–orbit coupling. Caldwell et al.[38] have calculated spin–orbit coupling (SOC) matrix elements for alkenes and have found that SOC indeed varies greatly with the angle of twist around the C=C bond. It was found that SOC is zero at the 90° geometry and is maximal at twist angles of 45 and 135°. Furthermore, pyramidalization at one of the trigonal centers (which removes the D_{2d} symmetry in the case of ethylene) also improves SOC, but the effect is not as large as that due to twisting. For 1-phenylcyclohexene, the geometry that simultaneously minimizes the T_1–S_0 gap and optimizes SOC was suggested to be that shown in structure **13**.[27]



13



14

By analogy, we suggest that, for 2-cyclohexenones, the T_1–S_0 gap is minimized and SOC is optimized in structure **14**. Thus, those cyclic enone triplets that can most closely approach structure **14** should have the shortest lifetimes. The results are in good agreement with this proposal. For TE, TA, and particularly the rigid bicyclononenones **9**, the T_1–S_0 gap is large and SOC is poor, resulting in relatively long triplet lifetimes. Intermediate effects are observed with phenanthrone (**8**) and octalone (**10**), which are conformationally more flexible than the analogous steroidal enones. While substitution of two methyl groups at C-4 of cyclohexenone has absolutely no effect on the triplet lifetime, alkyl substitution at C-3 leads to a significant increase in τ_T. The increase in τ_T due to methyl and ethyl substitution at C-3 is about the same, as anticipated on the basis of structure **14**, whereas a larger effect is seen upon *tert*-butyl substitution. Since there should be some reluctance to adopt a conformation analogous to **14** with an axial *tert*-butyl group, it is likely that, in this case, some alternative distortion of the six-membered ring occurs. The fact that substitution of a methyl group at C-2 has a much smaller effect on triplet lifetime than substitution at C-3 is also consistent with this model. The triplet lifetime of 103 ns for 2,3-DMCH (Table I) suggests that the effect of methyl substitution at both C-2 and C-3 on τ_T is multiplicative.

It is important to stress that structure **14** is not necessarily the energy minimum on the T_1 potential surface of cyclohexenones but rather represents the conformation for which T_1–S_0 radiationless decay is predicted to be optimal. Cyclopentenone (CP) is incapable of adopting such a twisted structure and therefore has a significantly longer limiting triplet lifetime than cyclohexenone (CH). In the case of CP, SOC may be promoted by pyramidalization at the β-carbon, perhaps accompanied by a modest degree of torsion around the C=C bond.

Excitation Energies of Enone Triplets from Transient Absorption Spectroscopic Data. This model predicts that the energies of relaxed T_1 states of flexible enones should be considerably lower than those of planar enone triplets. This hypothesis is supported by the variation in the rate constants (k_q) for quenching of enone triplets by NA (E_T 60.9 kcal/mol) and MN (E_T 59.6 kcal/mol) given in Table I. The highest values of k_q are observed for triplets of the rigid enones **4**, **6**, and **9**, and these approach the diffusion-controlled limit of ca. 5×10^9 M^{-1} s^{-1} in acetonitrile. This places the triplet energies of these enones substantially above 61 kcal/mol. Significantly lower rate constants were found for quenching of triplet states of CH (**5**) and diMeCH (**7**) by NA and MN. It was established that triplet energy transfer is irreversible in these cases since k_q is independent of enone concentration (up to 0.08 M). Since neither biphenyl (E_T 65.8 kcal/mol) nor phenanthrene (E_T 62 kcal/mol) quenched triplets of **7**, E_T of this enone is estimated to be 61–63 kcal/mol. This is substantially below the triplet energy of the "rigid" enones, assuming the variations in k_q are related only to changes in E_T.[39] The lifetimes and k_q values for 2-MeCH, 3-MeCH, and 3-EtCH suggest that these enones have triplet energies intermediate between these extremes. The correlation between τ_T and k_q fails for 3-tBuCH, perhaps because of steric inhibition of triplet energy transfer. However, steric effects on triplet energy transfer have been shown to be relatively small, except in cases where the π-systems of either the donor or the acceptor is twisted, thereby interfering with orbital overlap.[40]

It was clearly desirable to have independent verification of this hypothesis by direct measurement of the triplet energies of these cyclic enones. Direct singlet to triplet absorption and phosphorescence studies of steroidal enones at low temperatures established[41] that the lowest triplet states of these enones at 77 and 4.2 K is a $^3(\pi,\pi)^*$ state. For testosterone acetate (**6b**) in a single crystal, the 0–0 phosphorescence band occurs at 404.2 nm (70.8 kcal/mol). For testosterone itself (**6a**), the triplet energy is 71.2 kcal/mol. From the vibronic structure and polarization of the low-temperature phosphorescence spectra, it was concluded[41c] that, at low temperatures, the $^3(\pi,\pi)^*$ state of these steroidal enones is essentially planar. The only steroid enone for which T_1 was clearly a $^3(n,\pi)^*$ state was a derivative of 5-cholestenone (**15**), in which the enone moiety is incorporated into the B ring of the steroid system.[41d]

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(36) Trie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969.

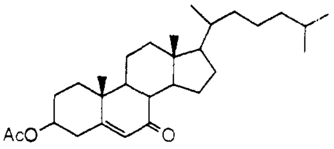
(37) Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5160.

(38) Caldwell, R. A.; Carlacci, L.; Doubleday, C. E., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 6901.

(39) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 328 ff. Lamola, A. A.; Turro, N. J. *Energy Transfer and Organic Photochemistry*; Interscience/Wiley: New York, 1969; Chapter II.

(40) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806 and references cited therein.

(41) (a) Jones, C. R.; Kearns, D. R. *J. Am. Chem. Soc.* **1977**, *99*, 344. (b) Marsh, G.; Kearns, D. R.; Schaffner, K. *Ibid.* **1971**, *93*, 3129. (c) Marsh, G.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1968**, *51*, 1890. (d) Jones, C. R.; Kearns, D. R.; Wing, R. M. *J. Chem. Phys.* **1973**, *58*, 1370.

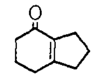
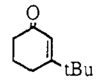
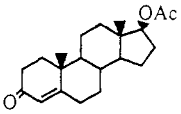
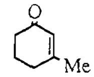
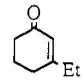
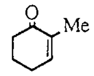
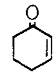
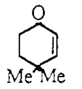
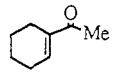
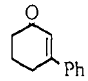
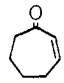


15

Correlation of Triplet Excitation Energies and Triplet Lifetimes of Cyclic Enones from Transient Absorption Spectroscopy (TAS) and Time-Resolved Photoacoustic Calorimetry (PAC). (a) Introduction. The PAC technique has been successfully applied to obtain accurate energies of nonemissive electronic excited states with lifetimes of 10–1000 ns[42] and of metastable ground-state molecules such as *trans*-1-phenylcyclohexene.[43] In collaboration with Professor Richard A. Caldwell at the University of Texas at Dallas, the PAC technique was used to determine both triplet lifetimes and triplet energies of a series of cyclic enones.[44-46] The data summarized in Table IV were obtained by assuming that intersystem crossing takes place with unit quantum efficiency within 0.1 ns.[47]

(b) Comparison of Enone Triplet Lifetimes from TAS and PAC Studies. There is generally excellent agreement between the enone triplet lifetimes determined by the PAC[44] and TAS techniques, verifying that indeed the same intermediates are being observed by both techniques. This agreement is particularly striking for CH (**5**), diMeCH (**7**), 2-MeCH, 3-MeCH, and 3-*t*-BuCH, where even the small solvent effects on triplet lifetimes revealed in the TAS studies are nicely reproduced by the PAC measurements. Speculation on the origin of these solvent effects has to await the collection of more data, although there appears to be a trend to longer triplet lifetimes in polar protic vis a vis polar aprotic and nonpolar solvents.

Table IV. Energies and Lifetimes of Triplet States of Cyclic Enones Determined by Time-Resolved Photoacoustic Calorimetry[39]

		triplet lifetimes, ns	
	E_T, kcal/mol	PAC	TAS
	73.8 ± 2.1, MeCN	383 ± 18	1460 ± 200
	70.1 ± 1.1, MeCN	140 ± 2	156 ± 4
	70.3 ± 0.7, MeCN	335 ± 21	387 ± 5
	71.1 ± 0.6, MeOH	82.3 ± 0.9	
	70.7 ± 2.3, C_6H_{12}	61.4 ± 1.2	62.3 ± 1.9
	68.7 ± 1.1, MeCN	74.3 ± 1.2	74.7 ± 2.1
	66.9 ± 1.0, MeCN	76.6 ± 3.6	67.5 ± 2.8
	66.7 ± 2.4, MeCN	50.7 ± 1.6	50.9 ± 2.0
	63.3 ± 1.6, C_6H_{12}	25.7 ± 0.4	25.8 ± 0.5
	63.2 ± 1.0, MeOH	35.7 ± 0.5	32.8 ± 1.0
	62.7 ± 1.0, MeCN	29.5 ± 0.6	30.3 ± 0.6
	63.6 ± 0.7, C_6H_{12}	23.2 ± 1.2	23.4 ± 1.4
	63.2 ± 1.5, MeOH	31.7 ± 0.6	30.9 ± 1.4
	63.3 ± 1.8, MeCN	26.6 ± 0.6	27.6 ± 1.9
	56.2 ± 7.6, MeCN	12.1 ± 1.9	12
	54.7 ± 0.1, MeCN	1470 ± 340	2760 ± 60
	43.2 ± 15.5, MeCN	10 ± 20	5

There is a small discrepancy between the TAS and PAC lifetime values for TA (**6b**) and a much larger one for BNEN (**9a**), although for both enones τ_T is significantly longer than for the monocyclic enones. In both cases, the triplet decay in TAS studies is biexponential, and there is clear evidence for triplet self-quenching. For BNEN (**9a**), a limiting triplet lifetime of 1.5 ± 0.2 μs in acetonitrile was obtained from direct TAS measurements as well as from extrapolation to infinite dilution of rates for quenching by oxygen NA, MN, and cyclopentene. This value for τ_T is much higher than that obtained from the PAC measurements, probably because the BNEN concentration used in the PAC study (0.08 M) was necessarily higher than that used in the TAS studies (0.03–0.06 M). One source of error in the PAC studies of BNEN is the large fraction of the excitation energy (337 nm, 84.8 kcal/mol) that is not returned as heat within the 2-μs observation window of the experiment.[46] This can be reconciled with the detection and identification of a long-lived intermediate in the TAS studies of this compound.[48] Another factor that should be considered is whether oxygen was rigorously excluded from the BNEN solution by the nitrogen flushing procedure employed in the PAC study. However, this procedure appears to have been adequate for the other PAC measurements, and reproducible lifetimes in the microsecond range have been obtained in other PAC studies using nitrogen-flushed solutions.[49]

A long triplet lifetime was found for 3-phenylcyclohexenone (3-PhCH) in both TAS and PAC studies, although due to the factors discussed above, the quantitative agreement is poor. A value of 2.0 μs for τ_T for this enone in cyclohexane has recently been reported by Kelly et al.[21] At the other end of the scale, the very short triplet lifetimes of acetylcyclohexene (**1**) and cycloheptenone (**3**) observed in early TAS studies[4,7] are confirmed by the PAC data.[44] In these cases, the poor quantitative agreement can be attributed to the relatively large errors associated with measuring lifetimes (ca. 10 ns) approximating the width of the laser pulse. In these systems, the observed heat discrepancy[46] is consistent with the production of relatively long-lived ground-state

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[42] For a review of the literature, see: Peters, K. S.; Snyder, G. J. *Science* **1988**, *241*, 1053. Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464. Lavilla, J. A.; Goodman, J. L. *Chem. Phys. Lett.* **1987**, *141*, 149.

[43] Goodman, J. L.; Peters, K. S.; Misawa, H.; Caldwell, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 6803.

[44] Schuster, D. I.; Heibel, G. E.; Caldwell, R. A.; Tang, W. *Photochem. Photobiol.* **1990**, *52*, 645.

[45] Melton, L. A.; Ni, T.; Lu, Q. *Rev. Sci. Instrum.* **1989**, *60*, 3217.

[46] The analysis of the signal in the PAC studies[44] is based on a paradigm in which the laser excitation energy (nitrogen laser, 337 nm, 84.8 kcal/einstein) is considered to be evolved as heat in two steps: (1) formation of the T_1 state and (2) decay of the T_1 state. The kinetics of these two processes are given by the lifetimes τ_1 and τ_2, respectively, and the fraction of the energy given off as heat in each step as ϕ_1 and ϕ_2. The values of τ_1 is set as either 0.1 or 1.0 ns, on the basis of previous studies,[1,2,4] and the other three parameters are allowed to float freely to provide the best fit to the experimental data. In most cases, the sum of ϕ_1 and ϕ_2 was unity within experimental error, indicating no intermediate or product with substantial heat content and a lifetime >2000 ns was formed in the system under the reaction conditions. In those cases where the sum of ϕ_1 and ϕ_2 was less than unity, there is a heat discrepancy due to the presence of such a species, e.g., a trans isomer of the starting enone, a long-lived dimeric triplet 1,4-biradical, or some other strained reaction product.

[47] Bonneau[4] reported that the transient absorption for the triplet of testosterone (**6a**) in ethanol grew in over ca. 20 ns, while the absorption of the other enone triplets was fully developed within the response time of the analytical system, i.e., <5 ns. We did not observe a slow rise time for appearance of the transient absorption of either testosterone acetate (**6b**) or BNEN under our experimental conditions, and fluorescence of these enones could not be detected.

[48] Woning, J.; Schuster, D. I.; Barra, M., submitted for publication.

[49] Arnaut, L. G.; Caldwell, R. A.; Melton, L. A. Private communication of unpublished results.

trans-enones[3,7,8] and can be used to estimate the strain energy of such compounds.[43,44]

(c) Enone Triplet Energies. The general agreement between the transient lifetimes measured by the PAC and TAS techniques lends credence to the enone triplet energies (E_T) given in Table IV. For the most part, these values are in excellent agreement with the estimates of E_T made above from the TAS data. Apart from the case of 3-PhCH, the longer triplet lifetimes are associated with higher triplet energies. This is the strongest evidence to date that the flexibility of the system with respect to torsion around the olefinic bond is the principal structural parameter that effects enone triplet energies and lifetimes. It is noteworthy that the value of E_T for TA is equal within experimental error to that derived from low-temperature spectroscopic data.[41] Hence, it can be concluded that the T_1 π,π^* state of TA is essentially planar both in solution at room temperature as well as in matrices at low temperatures.

From these data, it is also obvious that torsion around the C=C bond is not the only structural determinant of enone E_T values. The increase in E_T for the 3-alkylcyclohexenones relative to cyclohexenones lacking substituents on the double bond (CH and 4,4-diMeCH) suggests that pyramidalization at the β-carbon atom of the enone chromophore (see structure **14**) is also a significant relaxation mode on the T_1 potential energy surface. This model also rationalizes why *tert*-butyl substitution at C-3 causes a significant increase in both triplet lifetime and E_T and why methyl substitution at C-2 has a smaller effect on E_T than methyl substitution at C-3. The only compound in Table IV that is known to form a ground-state trans isomer is 1-acetylcyclohexene.[3] Not surprisingly, this enone has a very low energy triplet, although the error in its E_T value is quite large due to the short τ_T.

The only exception to the correlations between E_T and τ_T is 3-PhCH. The PAC value of E_T for 3-PhCH (55 kcal/mol) is in excellent agreement with the spectroscopic value of 54–55 kcal/mol obtained in an ether–ethanol matrix at 77 K.[50] The fact that a 3-phenyl substituent has a much greater effect on both triplet lifetime and E_T than a 3-*tert*-butyl group suggests that the T_1 state of 3-PhCH resembles that of a styrene more than a cyclohexenone. For arylethylenes, it was observed that when the triplet energy is high, there is a driving force for twisting to achieve a perpendicular geometry.[16] On the other hand, when the triplet energy is relatively low, the perpendicular geometry becomes an energy maximum and twisting is inhibited.[23,51] By analogy, there would be no driving force for twisting in the low-energy T_1 state of 3-PhCH, leaving the chromophore essentially planar and causing the lifetime to be on the order of that of a planar arylethylene.[16,51] Kelly[21] suggested that the long triplet lifetime of 3-PhCH is caused by severe 1,3-interactions that inhibit adoption of the twisted conformation, combined with the effects of conjugation between the phenyl and enone chromophores. The fact[21] that the limiting τ_T for 3-phenylcyclopentenone is even longer (20 μs) than for 3-PhCH supports these suggestions.

Quenching of Enone Triplets by Dienes. The interaction of enone triplets with 1,3-dienes remains puzzling. Rate constants for quenching of enone triplets by piperylene (E_T 57–59 kcal/mol) reported previously,[4] and the present k_q values for quenching by 2,5-dimethyl-2,4-hexadiene (E_T 57.2 kcal/mol)[27] determined by TAS at 280 nm, are summarized in Table III. Rigid high-energy enone triplets (e.g., **6a** and **9b**) are quenched by dienes at rates close to the diffusion-controlled limit and display linear Stern–Volmer plots. On the other hand, the Stern–Volmer plots for quenching of the triplets of enones **3**, **5**, and **7** by these dienes show pronounced curvature. The estimated values of k_q at low quencher concentrations are 1–2 orders of magnitude below k_{diff}, much lower than expected on the basis of the relative triplet energies of the enone donor and the diene acceptor.

One possible complication is the fact both [2 + 2] and [4 + 2] photocycloaddition of 1,3-dienes to cyclohexenones and cyclopentenone compete with triplet energy in these systems.[35,52] While the details of the interactions of enone triplets and dienes have yet to be fully elucidated, it is clear that the assumption[5,22,53] that conformationally flexible 1,3-dienes quench monocyclic enone triplets at approximately diffusion-controlled rates is incorrect. As pointed out by Scaiano and Wagner,[40] it is precisely in cases where the π-system of either the donor or the acceptor is twisted that triplet energy transfer rates are expected to be markedly less than diffusion controlled, because of poor orbital overlap between the donor and the acceptor. Thus, the low rates of triplet transfer observed in these systems provide further evidence that the π-system in relaxed triplets of conformationally flexible cyclohexenones is twisted. It is not surprising that k_q values of 4.6×10^8 and 3.2×10^8 M^{-1} s^{-1} are observed for quenching of 3-PhCH triplets by *cis*- and *trans*-piperylene, respectively,[21] each 1 order of magnitude less than k_q for quenching of 3-PhCP triplets by these same dienes. A reviewer has suggested the possibility that triplet energy transfer from enones to dienes may be inherently slow for some unknown reason and that perhaps the larger rate constants for quenching by dienes of rigid enone triplets are due to a charge transfer interaction. This problem clearly deserves further attention.

Self-Quenching of Enone Triplets. (a) Cyclopentenone. Contrary to earlier findings,[4] cyclopentenone (CP) triplets undergo efficient self-quenching, with k_{sq} of 5.1×10^8 and 5.9×10^8 M^{-1} s^{-1} in acetonitrile and cyclohexane, respectively.[6] The associated kinetic parameters derived from the TAS studies[6] are consistent with those obtained from steady-state studies of CP photodimerization,[5] provided that the latter results are corrected for the overly high rate constant (10^{10} M^{-1} s^{-1}) assumed for triplet quenching by piperylene. Indeed, the efficiency of CP triplet self-quenching has rendered it impossible thus far to determine the triplet energy of monomeric CP triplets by PAC.[6]

(b) Cyclohexenone. Self-quenching of cyclohexenone (CH) triplets was not observed in the earlier[4] nor the present TAS study. No systematic trend toward shorter triplet lifetimes in the enone concentration range 0.30–1.2 M in hexane was observed. On the other hand, Wagner and Bucheck reported[5] that the quantum yield for CH photodimerization in acetonitrile increases from 0.06 to 0.20 upon increasing the CH concentration from 0.25 to 1.00 M. These results appear to be mutually incompatible, unless the CH triplet observed in the TAS experiments is not the reactive intermediate in the photodimerization reaction, contrary to the case of cyclopentenone (see above). If Wagner's[5] k_{sq} value for CH of 1.1×10^8 M^{-1} s^{-1} were correct, CH self-quenching should have been observed, even with a limiting CH triplet lifetime of 25 ns. However, correction of Wagner's kinetic parameters using a lower, more realistic rate of CH triplet quenching by piperylene gives values for k_{sq} and for the limiting CH triplet lifetime in acetonitrile that are in much better agreement with our TAS and PAC data. Using our value (30 ns) for the CH triplet lifetime, a value for k_{sq} in acetonitrile of 1.1×10^7 M^{-1} s^{-1} can be calculated from the steady-state data, indicating that triplet self-quenching is more than 1 order of magnitude slower for CH than for CP. Increasing the CH concentration from 0.25 to 1.2 M would reduce the CH triplet lifetime from 25 to 20 ns, which is too small to be unambiguously detected by TAS. We therefore conclude that our failure to observe CH self-quenching in the TAS experiments does not rule out a twisted CH triplet (i.e., the 280-nm transient) as the reactive intermediate in CH photodimerization. Data from picosecond flash experiments are probably required to resolve this issue.

(c) 4,4-Dimethylcyclohexenone (7). Similar considerations as above apply in the case of this enone. Head-to-head and head-to-tail photodimers of **7** have been isolated and characterized.[35] The formation of the two dimers is differentially quenched by piperylene, and once again the Stern–Volmer plots are nonlinear. Hence, it was not possible to obtain kinetic parameters for comparison with the TAS data. However, if k_{sq} for this enone is also

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(50) McCullough, J. J.; Ramachandran, B. R.; Snyder, F. F.; Taylor, G. N. *J. Am. Chem. Soc.* **1975**, *97*, 6767.

(51) Bonneau, R. Unpublished results.

(52) Cantrell, T. S. *J. Org. Chem.* **1974**, *39*, 3063.

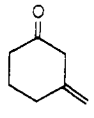
(53) Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559.

on the order of 10^7 M^{-1} s^{-1}, the failure to observe reduction in τ_T in the TAS studies as a function of increasing enone concentration can be rationalized.

(d) Other Cyclohexenones. For 3-PhCH in cyclohexane, Kelly[21] observed triplet self-quenching with $k_{sq} = 1.0 \times 10^7$ M^{-1} s^{-1}, consistent with the k_{sq} values for the cyclohexenones discussed above. Triplet self-quenching is also clearly detectable in the cases of testosterone acetate (**6b**) and BNEN (**9a**) because of their long triplet lifetimes. Although self-quenching could be due in principle to trace impurities, it was also observed with a rigorously purified sample of BNEN.[48] Self-quenching of 3-MeCH triplets could not be detected by TAS, but dimers of this enone are formed in steady-state irradiations.[15,54]

Residual Long-Lived Transition Absorption. As mentioned in the Results section, slowly decaying residual transient absorption amounting to 5–10% of the maximum transient optical density at the analyzing wavelength was observed for several enones. The identity of the species causing this residual absorption has not been determined. For testosterone acetate (**6a**) and BNEN (**9a**), the relative amount of residual absorption increased with increasing enone concentration, indicating it is due to one or more species produced in a second-order process. Although a dimeric triplet 1,4-biradical is an obvious possibility, the very long lifetime (in the microsecond range) of these transients argues against such an assignment; thus, the lifetime of the dimeric triplet 1,4-biradicals in the case of cyclopentenone is only 37 ns.[6]

Unlike TA and BNEN, 3-MCH and 3-EtCH undergo photodeconjugation to give β,γ-enones such as **16**, a reaction which is enhanced in the presence of trace amounts of acids.[54,55] Because extinction coefficients for UV absorption of β,γ-enones such as **16** in the n,π^* region (280–320 nm) are known to be much larger than those of isomeric α,β-enones,[56] such photorearrangement products were possible candidates for the residual absorption seen in the flash studies. Countering this is the fact that residual absorption is also seen in the case of 3-*tert*-butylcyclohexenone, which cannot undergo such isomerization. To account for the residual absorption observed at 280 nm for 3-MCH in terms of formation of **16**, the quantum yield would have to be at least 0.20, while the maximum quantum yield for deconjugation in the presence of added acid is only ca. 0.04.[54,55] Thus, the origin of the long-lived residual absorption following monomeric triplet decay of these 3-alkylcyclohexenones remains unclear.



16

Conclusions

Upon excitation with a laser pulse under a variety of conditions, cyclic enones produce transient intermediates with lifetimes usually in the nanosecond domain, which display absorption in the 270–400-nm region with λ_{max} 280–310 nm. The variations with molecular structure of the lifetimes of these intermediates and of the rate constants for quenching by triplet quenchers support the assignment of these enone transients as relaxed twisted triplet excited states. This assignment was confirmed by studies using time-resolved photoacoustic calorimetry, which directly afforded energies of these enone triplets under ambient conditions. On the basis of their energies and lifetimes, it is concluded that the triplet states of steroid enone and fused ring enones such as BNEN are essentially planar (long lifetimes, high S_0–T_1 energies), while the triplets of simple cyclohexenones are highly twisted (short lifetimes, lower S_0–T_1 energies). Additional geometric distortion of cyclohexenone triplets by pyramidalization at the β-carbon of the enone moiety could explain the observed increase in triplet lifetimes and energies observed when substituents of increasing bulk are introduced at this carbon atom. Rates of quenching of the flexible enone triplets by dienes are anomalously low for reasons that remain to be elucidated, as do the nature of the long-lived secondary transients seen in most systems.

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Registry No. 4, 930-30-3; **5**, 930-68-7; **6a**, 58-22-0; **6b**, 1045-69-8; **7**, 1073-13-8; **8**, 79147-45-8; **9a**, 22118-01-0; **9b**, 73013-93-1; **10**, 1196-55-0; **11**, 32264-57-6; 2-methylcyclohexenone, 1121-18-2; 3-methylcyclohexenone, 1193-18-6; 3-ethylcyclohexenone, 17299-34-2; 2,3-dimethylcyclohexenone, 1122-20-9; 3-*tert*-butylcyclohexenone, 17299-35-3; 3-phenylcyclohexenone, 10345-87-6.

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