Photophysics of enediones

Luiz H. Catalani, Vicente G. Toscano and Ivan P. de Arruda Campos *,†
Instituto de Química, Universidade de S. Paulo, Cx.P. 26.077, 05599-970, S. Paulo, SP, Brazil

Monocyclic and acyclic 2-ene-1,4-diones have been investigated by electronic absorption and luminescence emission spectroscopies, as well as by the laser flash-photolysis technique (enedione triplet–triplet transient absorptions being observed). The energies of the three lowest excited singlet and of the lowest excited triplet states were determined. The observation of fluorescence emission from enediones (in EPA glass at 77 K) is reported for the first time.

In 1906, Albrecht[1] obtained the first known enedione from the reaction of benzoquinone with cyclopentadiene. However, it was only in 1928 that Diels and Alder[2] established the correct structure of the benzoquinone–cyclopentadiene adduct (1). Later, Alder and Stein[3] recognized that the adduct 1 could present two isomers: *endo* (1a) and *exo* (1c), depending on the stereochemistry of the newly formed ring-junction. In 1964, Cookson *et al.*[4] observed that, under UV irradiation, the benzoquinone–cyclopentadiene adduct undergoes isomerization to a cage compound (2a). They reasoned that only the

1

1a R = H
1b R = Me

1c

1d

1e

2a R = H
2b R = Me

3

4

5

6

7

8

9a R = R′ = H
9b R = H; R′ = Me
9c R = R′ = Me

endo-adduct 1a could undergo photocyclization to form compound 2a, actually elucidating the stereochemistry of the enedione 1. Since then, the photocyclization reaction has become a widely used criterion for structural assignment: its

observation is accepted as proof that the irradiated compound is of *endo*-configuration. On the other hand, failure to undergo photocyclization does not necessarily indicate the presence of the *exo*-configuration, because, as demonstrated by Wladislaw *et al.*,[5] there are some substituted benzoquinone–cyclopentadiene *endo*-adducts that do not form cage compounds upon irradiation.

Polycyclic enediones are also fundamental components of two different chemical solar-energy storage systems, both proposed by Mehta *et al.*,[6] in the last decade.

Dilling[7a] was the first to point out that the excited species involved in the photocyclization of adduct 1a is a triplet state of the enedione which, upon reaction with the norbornenic double-bond carbons, should generate a biradical intermediate (1e). This intermediate would then collapse to form the cage compound 2a. Moreover, the comprehensive investigation on the photochemistry of adducts of benzoquinone with acyclic dienes, by Sheffer and Trotter,[7b] provides strong evidence in favour of the involvement of biradicals as intermediates: their adducts, not having a methano- or ethano-bridge in the molecules, are much more flexible and thus, instead of photocyclization, the observed process in solution is γ-hydrogen-atom abstraction, followed by cyclization of the rearranged biradical.
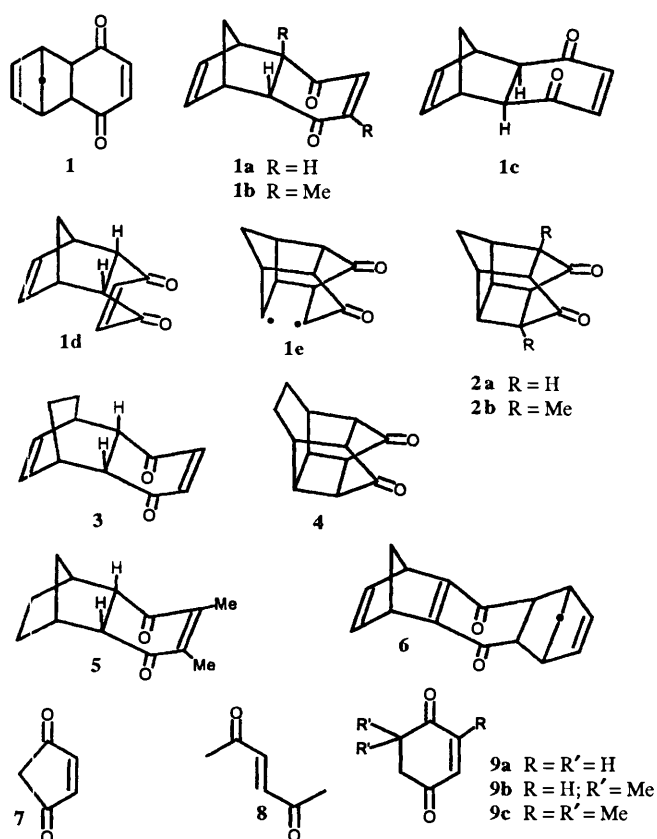
Barltrop and Giles,[7c] in a study of the related addition reaction of polycyclic enediones to olefins, proposed a similar pathway, from triplet through biradical to cyclobutane. They demonstrated the involvement of a triplet state by means of quenching experiments and determined, from the phosphorescence emission spectrum of enedione 5, its ΔE_{0-0}^3 (T$_1$). Further evidence in favour of the involvement of a triplet state has been provided by the recent quenching and laser flash-photolysis spectroscopic studies reported by Mehta *et al.*,[6b] for the case of some polycyclic enediones (both isomers of 6 and four derivatives).

All this is consistent with the contemporary view[8] that photochemical reactions involving triplet states are not concerted and lead to the formation of biradical intermediates.

As most of the existing (and rather scattered) photophysical data on enediones was obtained from enedione chromophores present within rather complex molecular structures, most of which possess at least one remote double bond (non-conjugated to the enedione system), we found it of interest to perform an investigation on the photophysics of enediones in which the substracts should be the simplest possible compounds, bearing, as the only functional group, the chromophore under study.

Results and discussion

The search for simple enediones led us to select as substrates for our investigation the following compounds: cyclopent-4-ene-1,3-dione (7), (*E*)-hex-3-ene-2,5-dione (8), cyclohex-2-ene-
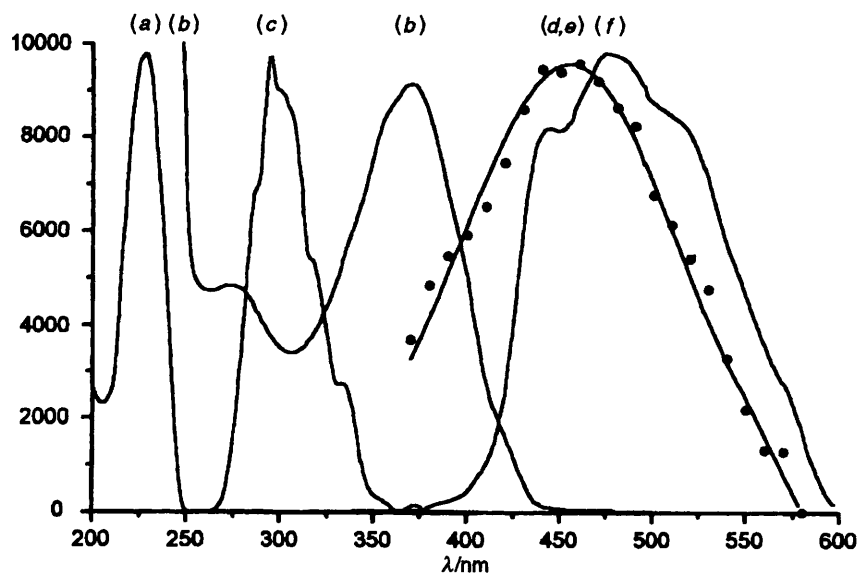
Fig. 1 (a) UV–VIS absorption spectrum of **9b** in isooctane, at 293 K (the ordinate is $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$); (b) UV–VIS absorption spectrum of **9b** in isooctane, at 293 K (expansion plot: the ordinate is $\varepsilon \times 200\ dm^3\ mol^{-1}\ cm^{-1}$); (c) fluorescence emission spectrum of **9b** in EPA glass, at 77 K (excited at 250 nm; the ordinate is in arbitrary intensity units); (d) transient absorption spectrum of **9b** in deaerated benzene, at 293 K (photolysed with 355 nm Nd:YAG laser; the ordinate is $\Delta A \times 8.3 \times 10^5$); (e) gaussian fit of the transient absorption spectrum of **9b** in deaerated benzene, at 293 K (same as above); (f) phosphorescence emission spectrum of **9b** in EPA glass, at 77 K (excited at 330 nm; the ordinate is in arbitrary intensity units)

Table 1 UV–VIS absorption data of enediones[a]

| Compd. | λ/nm (log[$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$]) | | | Solvent |
	$\pi \longrightarrow \pi^*$ $(S_0 \longrightarrow S_3)$	$[n + n] \longrightarrow \pi^*$ $(S_0 \longrightarrow S_2)$	$[n - n] \longrightarrow \pi^*$ $(S_0 \longrightarrow S_1)$	
7	215 (4.12)	288 (1.37)	384 (1.22)	Isooctane
	217 (4.09)[b]	259 (1.60)	359 (1.38)	Acetonitrile
8	226 (3.22)	288 (1.73)	315 (1.77)	Isooctane
	229 (3.95)[b]	—	310 (2.00)	Acetonitrile
9a	219 (4.20)	277 (1.34)	368 (1.78)	Isooctane
	223 (4.17)[c]	272 (1.71)	357 (1.81)	Acetonitrile
9b	228 (3.99)	273 (1.38)	370 (1.66)	Isooctane
	232 (3.97)[c]	268 (1.73)	354 (1.95)	Acetonitrile
9c	237 (4.10)	280 (1.21)	363 (1.79)	Isooctane
	240 (4.00)[c]	275 (1.69)	357 (1.87)	Acetonitrile
1a[d]	226 (4.11)	278 (2.40)	385 (1.75)	Cyclohexane
	226 (4.11)	284 (2.41)	374 (1.80)	Ethanol
3[d]	223 (4.11)	267 (2.51)	388 (1.81)	Cyclohexane
	227 (4.04)	278 (2.42)	376 (1.78)	Ethanol

[a] At 293 K. [b] In ethanol. [c] In methanol. [d] From ref. 4.

1,4-dione (**9a**), 5,5-dimethylcyclohex-2-ene-1,4-dione (**9b**) and 2,6,6-trimethylcyclohex-2-ene-1,4-dione (**9c**).

The spectra obtained from compound **9b**, by the various techniques employed in this work, are presented in Fig. 1 as typical representatives of the results obtained with the whole series.

Electronic spectra

Cookson et al.[4] were the first to investigate the UV absorption spectra of polycyclic enediones, which show three bands (Table 1). These authors assigned the first band to a $\pi \longrightarrow \pi^*$ transition, the third to an $n \longrightarrow \pi^*$ transition and the second band as arising from a charge-transfer between the norbornenic double bond and the enedione moiety. This latter assignment is

surprising, in view of the results of Modelli et al.[9] and of Paul and Kebarle,[10] on the ionization potentials and electron affinities of cyclopent-4-ene-1,3-dione (**7**) and related compounds, as they demonstrated that two filled non-degenerate non-bonding orbitals (labelled $[n - n]$ and $[n + n]$) lie above the highest filled π orbital in those molecules.

Hence, probably, the best assignments for the observed UV–VIS absorption bands should be $\pi \longrightarrow \pi^*$, $[n + n] \longrightarrow \pi^*$ and $[n - n] \longrightarrow \pi^*$, in order of decreasing energy. If so, three bands should be observed even in compounds that do not have a remote double bond to serve as charge-transfer donor.

The UV absorption data for compounds **7–9** are also presented in Table 1. Three bands were observed, in all cases, as

Table 2 Phosphorescence emission data of enediones[a]

	λ/nm		
Compd.	1st vb[b]	2nd vb[b]	τ_{Ph}/ms[e]
7	415[c]	444	1.0
8	(542)[d]	579[c]	2.6
9a	429	465[c]	2.3
9b	445	483[c]	3.1
9c	439	476[c]	2.1

[a] In EPA glass, at 77 K. [b] Vibrational band. [c] λ_{max}. [d] Estimated value. [e] ±10%.

expected. We have assigned these absorption bands, in order of decreasing energy, to the transitions $\pi \longrightarrow \pi^*$ ($S_0 \longrightarrow S_3$), $[n + n] \longrightarrow \pi^*$ ($S_0 \longrightarrow S_2$) and $[n - n] \longrightarrow \pi^*$ ($S_0 \longrightarrow S_1$), in accordance with our reasoning in the previous paragraph.

It must be pointed out that the $S_0 \longrightarrow S_2$ transition of enediones 7–9 have ε values of a magnitude comparable to those of the $S_0 \longrightarrow S_1$ transition, a fact consistent with the present assignments. All the polycyclic enediones investigated by Cookson et al.,[4] on the other hand, present ε values ca. five times greater at the $S_0 \longrightarrow S_2$ than at the $S_0 \longrightarrow S_1$ transition. This observation may be an indication that, in that case, either there really is a charge-transfer band overlapping the $S_0 \longrightarrow S_2$ transition or, more likely, that there is a through-bond (TB) interaction[11] with the remote double bond operating in those benzoquinone–diene adducts (especially as their preferred conformation, in solution, is the 'open'-conformer[12a] 1a, whereas only the 'closed'-conformer 1d, which contributes very little to the total population, would have an inter-double-bond distance short enough for some through-space interaction, i.e., for charge-transfer). The TB interaction might also account for the solvent effects apparently incompatible with a $n \longrightarrow \pi^*$ transition, observed by Cookson et al.,[4] which led them to assign the intermediate energy band as being due to a charge-transfer absorption.

We did not observe any unusual solvent effects on the intermediate energy band, in the spectra of enediones 7–9: in fact, in methanol and in ethanol, it seems to vanish, because, as both $n \longrightarrow \pi^*$ transitions undergo hypsochromic displacement (measured as ca. 10 nm at the $[n - n] \longrightarrow \pi^*$ band), the $[n + n] \longrightarrow \pi^*$ band becomes hidden under the much more intense $\pi \longrightarrow \pi^*$ absorption. Moreover, in acetonitrile, the enediones 7 and 9a–c do exhibit the expected hypsochromic shift at both $n \longrightarrow \pi^*$ transitions, although the $[n + n] \longrightarrow \pi^*$ band remains unresolved from the $\pi \longrightarrow \pi^*$ absorption, for enedione 8.

Luminescence spectra and the energies of excited states

No luminescence whatsoever was observed from degassed isooctane solutions of the enediones 7–9, at room temperature.

The phosphorescence emission spectra of compounds 7–9 (excited at 330 nm) were obtained at 77 K, in EPA glass. Vibrational fine structure was observed in all cases, except for 8, the emission spectrum of which is a single featureless band. Phosphorescence lifetimes (τ_{ph}) were also measured, in the same conditions. The emissions' intensities decay according to first-order kinetics, over milliseconds. The phosphorescence data are summarized in Table 2.

We have estimated the energies (ΔE_{0-0}) of the first, second and third excited singlet states (from the lower-energy onsets of the respective $S_0 \longrightarrow S_n$ UV absorption bands) and the energy of the first excited triplet state (from the highest-energy vibrational band of the phosphorescence emission spectra) for compounds 7–9, which are presented in Table 3.

While there is no previously published data on the singlet energies of enediones, our data (for the six-membered ring

Table 3 Energies of the excited states of enediones[a]

Compd.	ΔE_{0-0}^1 (S_3)	ΔE_{0-0}^1 (S_2)	ΔE_{0-0}^1 (S_1)	ΔE_{0-0}^3 (T_1)
7	116	96	72	70
8	106	97	74	53
9a	111	94	70	67
9b	109	94	69	64
9c	107	95	71	65
1a[b]	111	97	66	—
3[c]	113	97	66	60
5[d]	—	—	—	58
8[e]	—	—	—	≤55

[a] In kcal mol^{-1}, at 293 K. [b] From ref. 4. [c] From refs. 4, 12(b). [d] From ref. 7(c). [e] From ref. 13.

Table 4 Fluorescence emission data of enediones[a]

	λ/nm	
Compd.	1st vb[b]	2nd vb[b]
7	292[c]	301
8	292[c]	303
9b	288	295[c]
9c	286	292[c]

[a] In EPA glass, at 77 K. [b] Vibrational band. [c] λ_{max}.

enediones 9) are in line with the values (also in Table 3) that can be estimated from the UV spectra published by Cookson et al.[4] and with the literature values for the ΔE_{0-0}^3 (T_1) (for compounds 3 and 5). The ΔE_{0-0}^1 (S_1) and the ΔE_{0-0}^3 (T_1) for the enediones 7–9 are ca. 3–10 kcal mol^{-1} higher than those for the polycyclic enediones, the only exception being the ΔE_{0-0}^3 (T_1) of 8, which is 7 kcal mol^{-1} lower. It is worth mentioning that Yoshida et al.[13] have reached an upper-limit value of 55 kcal mol^{-1} for the ΔE_{0-0}^3 (T_1) of compound 8, through sensitized irradiation studies, which is in fair agreement with the ΔE_{0-0}^3 (T_1) we estimated from the highest-energy onset of the phosphorescence emission band from enedione 8.

In our opinion, all these differences in the magnitude of the energy values are attributable to strain and conformational variations at the enedione chromophore. According to our own MM$^+$ calculations (HyperChem 3), the enedione moiety is planar in compounds 7 and 8 (but only in the latter it is free of angular strain); in the cyclohexenediones 9, the carbonyls are slightly bent from the double-bond plane (in opposite directions), as these rings adopt chair-like preferred conformations while, in the polycyclic enediones, the six-membered rings containing the chromophore, due to the cis ring-junction, must adopt boat-like conformations,[12a] therefore forcing the carbonyls to be slightly bent off the double-bond plane (both in the same direction).

Moreover, the observed phosphorescence lifetimes (τ_{ph}) in EPA glass (at 77 K) can also be explained: while enedione 7 has $\tau_{ph} = 1.0$ ms, the less strained compounds 9, along with the strainless 8, present τ_{ph} of 2.1–3.1 ms, although it is puzzling to observe that 9b, instead of 8, exhibits the longest τ_{ph}.

To our knowledge, there is no previous report on the observation of fluorescence emission from enediones. This notwithstanding, we did find a structured (albeit weak)‡ fluorescence emission band with maximum intensity at 286–295 nm (in EPA glass, at 77 K, excited at 250 nm) for enediones 7–9 (Table 4), except for compound 9a, for which, if it exists, it

‡ At the suggestion of one of the referees, we have determined, for enedione 9b, the quantum yields of fluorescence ($\Phi_F = 0.013$) and of phosphorescence ($\Phi_P = 0.032$), in EPA glass at 77 K, by the method of Demas and Crosby,[20a] with biphenyl[20b] as the standard, using optically matched solutions ($A = 0.9$) and $\lambda_{exc} = 245$ nm.
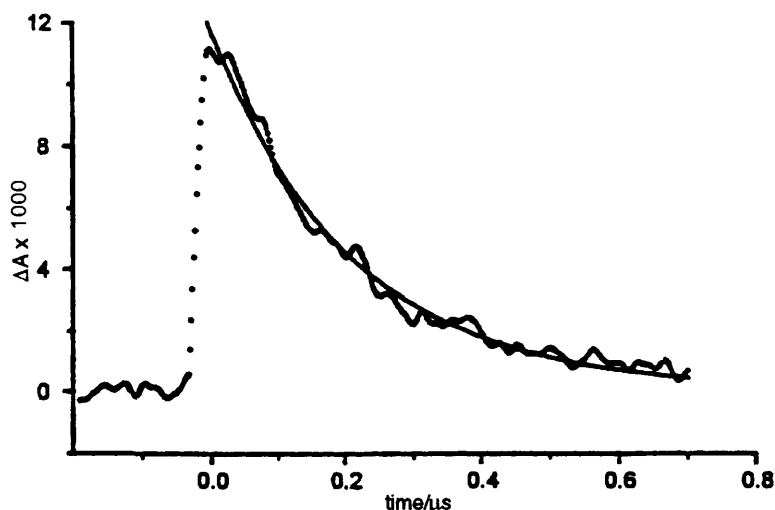
Fig. 2 Transient kinetic decay due to laser flash-photolysis of **9b** in deaerated benzene, at 293 K, with the 355 nm line of an Nd:YAG laser; detected at 460 nm, together with the fitted exponential decay curve

Table 5 Laser flash-photolysis data of enediones[a]

	Transient absorptions	
Compd.	λ_{max}/nm[b]	τ_T/µs[c]
7	465	0.27
8	450	2.53
9a	455	0.08
9b	455	0.21
9c	450	1.64

[a] In degassed benzene, at 293 K. [b] ±5 nm. [c] ±15%.

lies masked under the stronger fluorescence emission due to hydroquinone (an inevitable impurity, being the thermodynamically more stable tautomer of **9a**). The energies of the lowest-wavelength vibrational bands of the observed fluorescence emissions, when compared with ΔE_{0-0}^1 (S$_n$), show that this must be a case of S$_2$ ⟶ S$_0$ fluorescence.§ Although here the S$_2$–S$_1$ energy gap is relatively small (*ca.* 25 kcal mol^{-1}), it ought to be enough to slow down internal conversion, at 77 K, for the emission from S$_2$ to occur; the S$_2$–S$_1$ gap for azulene[14a] is 40 kcal mol^{-1}, and for aryl alkyl thioketones[14b] it ranges from 24 to 36 kcal mol^{-1}, being enough for those compounds to emit light from S$_2$ at room temperature, in degassed solution.

Transient absorption spectra

The T$_1$ ⟶ T$_n$ absorption spectra of compounds **7–9** were observed in degassed benzene solution, after flash-photolysis with a tripled (355 nm) Nd:YAG laser. The transients decay by clean first-order kinetics, over microseconds. When air was admitted into the cell, which was then shaken, the T$_1$ ⟶ T$_n$ absorption transients disappeared completely, as expected from the results by Mehta *et al.*,[6b] on oxygen quenching of the

§ We believe that the observed fluorescence emissions cannot be ascribed to the 0.5% impurities present in the enediones because, in all cases, these are mainly the synthetic precursors for each compound: an enediol for **7**, a γ-diketone for **8**, and the corresponding enones for **9b**, **c**, which do not present similar fluorescence emissions at all. The observed emissions, on the other hand, are very similar for all the enediones employed in this study. Moreover, while the phosphorescence excitation spectra for compounds **7–9** are essentially identical with the absorption spectra, the fluorescence excitation spectra fail to exhibit the bands corresponding to the S$_0$ ⟶ S$_1$ absorption bands, in all cases, as expected for emissions from higher excited states.[14b]

transients due to polycyclic enediones. The T$_1$ ⟶ T$_n$ absorption maxima and lifetimes (τ_T) are presnted on Table 5 and in Fig. 2; the kinetic trace due to the enedione **9b** transient is given as a representative example.

It must be pointed out that compounds **7** and **9** were recovered unchanged after being submitted to prolonged irradiation (24 h) in benzene solution, with Pyrex-filtered UV light from a medium-pressure mercury lamp, our GLC analyses revealing that not even traces of other products were formed. Compound **8**, on the other hand, is known[13] to undergo *cis–trans* isomerization, forming a 95% *cis-* and 5% *trans*-isomer mixture on attaining a photostationary state.

The enediones here investigated can be divided in two groups having different magnitudes of τ_T: those enediones possessing a *trans* substituent attached to the double bond (**8** and **9c**) present $\tau_T \approx 2$ µs, while the other compounds show *ca.* ten times smaller τ_T values. It appears, therefore, that steric hindrance of the triplet excited molecules is a major factor influencing τ_T in solution at room temperature (20 °C). Under these conditions, collisions with solvent molecules (and *cis–trans* isomerization, for **8**) are the main accessible mechanisms for relaxation of the excited molecules. Of course the variations in τ_T do not parallel those we observed before in τ_{ph}, because collisional deactivation cannot be important in EPA glass (at 77 K).

A comparison of our results with the T$_1$ ⟶ T$_n$ absorption data on polycyclic enediones[6b] appears to indicate that in those compounds there should indeed be some interaction between the chromophore and either one (or both) of their norbornenic double bonds as they present λ_{max} = 390–420 nm, in degassed benzene, while the simple enediones **7–9** have λ_{max} = 450–465 nm. Furthermore, polycyclic enediones show triplet lifetimes of 0.25–0.55 µs (except for the compounds bearing bromine substituents, for which $\tau_T \leqslant 0.08$ µs), although their enedione chromophore is subject to extremely efficient steric hindrance afforded by their adjacent norbornene moiety. There, however, deactivation of the excited states must proceed through photocyclization: indeed, cage compound formation has been reported[6b] for all but one of those polycyclic compounds, upon steady-state irradiation with Pyrex-filtered UV light from a medium-pressure mercury lamp.

Conclusions

From the data available in the literature one can ascertain that the photocyclization of **1a** to compound **2a** in solution proceeds

with quantum yields (Φ) of *ca.* 1.00 (at 260–300 nm)[15] and 0.79 (at 405 nm).[12b] For the related isomerizations of the dimethyl-derivative **1b** to **2b**, $\Phi = 0.98$ (at 362 $\pm$ 5 nm)[15b] and for the benzoquinone–cyclohexadiene adduct (**3**) to the cage compound **4**, $\Phi^{8a} = 1.00$ (at 313 nm), 0.81 (at 405 nm) and 0.15 (at 440 nm). It seems, therefore, reasonable to suppose that the quantum yields of photocyclization are unitary (or almost so) and independent of wavelength, if light with photon energy above 71 kcal mol^{-1} is employed. On the other hand, for Φ of photocyclization to be unitary (or almost), it is required that the quantum yields of triplet formation (Φ_T) also approach unity. In fact, this was found to be the case for Φ_T of the polycyclic enediones investigated by Mehta *et al.*[6b]

Galin *et al.*[12b] have determined an Arrhenius activation energy of (5.0 ± 0.5) kcal mol^{-1} for the photocyclization of **3** to **4**, by analysing the dependence on temperature of the quantum yield of product formation. If this activation energy is related to the 'open' (**1a**) to 'closed' (**1d**) conformational interconversion,[12a] it might imply that the interconversion actually takes place in an excited state, possibly the first excited triplet state (because of its longer lifetime, when compared with a singlet state), in the course of vibrational relaxation.

Assuming that, after light absorption, the 'open'-adduct **1a** will dissipate 5.0 kcal mol^{-1} to form a 'closed'-like triplet state, having ΔE^3_{0-0} (T_1) $= 60$ kcal mol^{-1}, and that the singlet–triplet separation[6b] is of 6 kcal mol^{-1}, one can estimate that a threshold photon energy of 71 kcal mol^{-1} (*ca.* 405 nm) would be necessary for Φ to be independent of λ, well in agreement with our proposal above.

Furthermore, as only one transient (characterized as the triplet enedione) was reported[6b] for each polycyclic enedione, the deactivation of the triplet (formation of **1e**, Dilling's biradical[7a]) must be the rate-controlling step in the photocyclization reactions, while the collapse of the biradical **1e** to form the cyclobutane ring of the cage compound has to be a quicker, subsequent process. It should also be pointed out that the formation of Dilling's biradical is a process that proceeds at a rate similar to that of the diffusional deactivation of simple enediones, as τ_T of the polycyclic enediones (except for those bearing bromo-substituents, see above) is comparable to that of the sterically unhindered enediones **7**, **9a** and **9b**.

Experimental

The enediones **7**,[16] **8**,[17] **9a**,[18] **9b**[19] and **9c**[19] were prepared according to literature procedures and recrystallized (at low temperature, when necessary) until 99.5% purity (by ^{1}H NMR spectroscopy and by GLC) was attained. Biphenyl (Carlo Erba) was twice recrystallized from *n*-hexane (Aldrich, *PA*). The EPA-mixed solvent (Matheson, Coleman & Bell) and all other solvents (Aldrich, Gold Label) were of spectrophotometric grade, and were used without prior purification.

Electronic absorption spectra were measured with a Hitachi U-2000 spectrophotometer, while a Spex Fluorolog-2 FL111 instrument (with a 1934D phosphorimeter and a sample-tube holder within a quartz Dewar flask for liquid nitrogen) was employed for the measurement of the luminescence emission spectra. All the luminescence spectra were corrected for the instrument response at all wavelengths. The flash-photolysis experiments were performed (on benzene solutions of the enediones, degassed to 5×10^{-5} Torr through five freeze–pump–thaw cycles) with an Applied Photophysics kinetic spectrometer having a tripled Nd:YAG laser (355 nm) for

excitation, a pulsed xenon short-arc lamp for monitoring the transients and a photomultiplier connected to a Techtronics 2230 oscilloscope for detection. A Bruker AC-200-F spectrometer was employed for measuring the ^{1}H NMR spectra at 200 MHz [in CDCl$_3$ solutions, δ_H(SiMe$_4$) $= 0$]. A Shimadzu GC-14-A chromatograph, using a splitter injector (80:1), a CBP-1 polydimethylsilicone gum capillary column (25 m $\times$ 0.25 mm $\times$ 0.22 µm), helium as carrier gas and a flame ionization detector connected to a Chromatopac C-R4A data processor, was employed for all GLC analyses.

The MM$^+$ molecular mechanics calculations were performed with HyperChem, Release 3 for Windows (Hypercube and Autodesk).

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