Photochemistry of substituted cyclic enones. Part 11.[1] Synthesis and photophysics of 5-arylalkyl-3-phenylcyclopentenones

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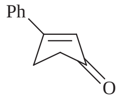
The photophysical properties of 3-phenyl-5-[2-(1-naphthyl)ethyl]cyclopent-2-enone and 5-[2-(1-naphthyl)-methyl]-3-phenylcyclopent-2-enone have been compared with those of their constituent alkylated chromophores 1-ethylnaphthalene, 3-phenyl-5-(2-phenylethyl)cyclopent-2-enone and 3-phenyl-5-benzylcyclopent-2-enone by means of UV absorption spectroscopy, steady state and time resolved low temperature emission spectroscopy and laser flash photolysis. In mixed solvent low temperature glasses such as ethanol–isopentane–diethyl ether (2 : 5 : 5, v/v) (EPA) phosphorescence decay of all the enones shows multiexponential behaviour consistent with different lifetimes at different solvent sites. The naphthalene derivatives also show a longer lived emission consistent with slow processes involving a naphthalene localised triplet excited state. By contrast in fluid solution flash photolysis experiments reveal that there is rapid equilibration between the enone- and naphthalene-localised states.

Introduction

The photochemical addition reactions of α,β-unsaturated ketones are an important class of synthetic procedures which can take place either intramolecularly or intermolecularly.[2] There is also interest in the mechanism of such reactions and there has been considerable discussion on the possible roles of exciplexes and biradical intermediates.[3,4] In this context 3-phenylcyclopent-2-enones are of interest as they undergo similar reactions and it has been shown that on excitation the parent compound **1** affords a triplet state which has an exceptionally long lifetime compared with those of other enones.[5] This may be caused by conjugation between the phenyl group and the enone which inhibits twisting in the excited state. This photophysical property makes it a most suitable mechanistic probe for many studies.



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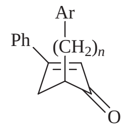


2 *n* = 1, Ar = phenyl
3 *n* = 2, Ar = phenyl
4 *n* = 1, Ar = 1-naphthyl
5 *n* = 2, Ar = 1-naphthyl

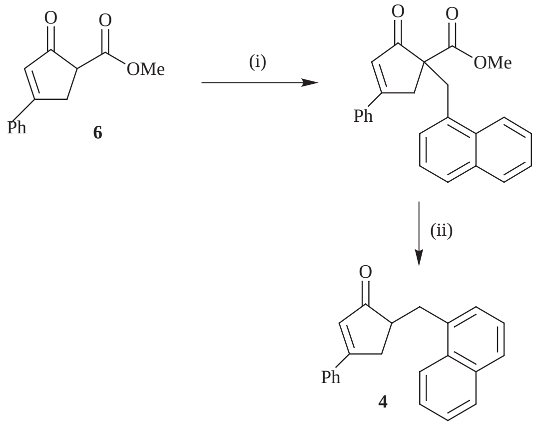
The intramolecular cycloaddition of enones to arenes, alkenes and alkyluracil has been studied in our laboratories.[6–8] In each of these systems it is possible to selectively excite the enone moiety. The efficiency of the reaction depends strongly on the nature of the arene and the chain length of the linker. Thus although there is no intramolecular cycloaddition product obtained from the 3-phenyl-5-benzylcyclopent-2-enone **2**, photolysis of the corresponding 5-(1-naphthylmethyl) compound **4** gives a cyclobutane photoproduct.[7]

In order to examine the effect of arene and chain length on the photophysical properties of such bichromophoric systems, we have synthesised 5-(2-phenylethyl)- and 5-[2-(1-naphthyl)-ethyl]-3-phenylcyclopent-2-enone, **3** and **5** respectively. In addition we report an alternative synthesis for **4** and photophysical measurements for **2** and **4**. In each case we have carried out laser flash photolysis and phosphorescence studies on these bichromophoric systems and compare the measurements with those of the parent enone **1** and naphthalenes.

Results

Synthesis

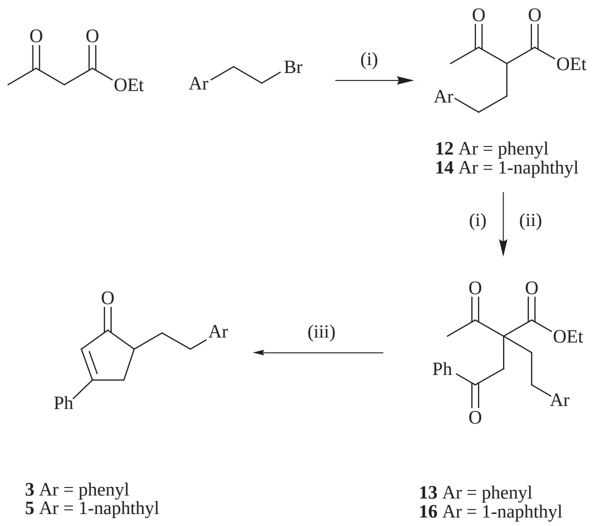
The 1-naphthylmethylcyclopentenone **4** was prepared by the alkylation/decarboxylation of the enone ester **6** following the method successfully used for synthesising enone-uracil bichromophoric derivatives (Scheme 1).[8] The 2-(1-naphthyl)ethyl- (**5**) and 2-phenylethyl- (**3**) cyclopentenones were synthesised according to the method described by Wilds and Johnson (Scheme 2).[9] Alkylation of the sodium enolate of ethyl 3-oxobutanoate by the appropriate arylethyl halide afforded the monoalkyl derivative which was reacted further with phenacyl bromide to give the ethyl 2-acetyl-2-(2-arylethyl)-4-oxo-4-phenylbutanoate. This was decarboxylated and cyclised with base to produce the cyclopentenone.



Scheme 1 *Reagents and conditions*: (i) 1,8-diazabicyclo[5.4.0]undec-7-ene, 1-chloromethylnaphthalene, xylene; (ii) NaOMe, NaOH, MeOH, H_2O

Ground state

The ground state absorption spectral data of compounds **1**–**5** in cyclohexane are presented in Table 1. Those of the phenylalkyl derivatives are similar to that of 3-phenylcyclopent-2-enone **1**, showing a π–π* absorption with a maximum at approximately 277 nm and a weak band in the region 320–360 nm, which can be ascribed to the n–π* transition. The spectra of the naphthyl



Scheme 2 *Reagents and conditions*: (i) NaH; (ii) $PhCOCH_2Br$; (iii) KOH, 1%, then 10%

Table 1 Ground state absorption spectral data of enones **1**–**5** and ethylnaphthalene **7** in cyclohexane and phosphorescence data in EPA glasses at 77 K

	Ground state	Excited state (emission spectroscopy)	
Comp.	λ_{max}/nm (log ε)	Principal bands/nm	E_T/ kJ mol^{-1}
1	274 (4.29)	480, 516, 556	249.2 ± 0.5
2	278 (4.33)	481, 517, 557	248.7 ± 0.5
3	276 (4.35)	480, 517, 557	249.2 ± 0.5
4	277 (4.44), 314 (sh) (2.93)	480, 517, 558	249.2 ± 0.5
5	278 (4.45), 314 (sh) (2.77)	480, 516, 557	249.2 ± 0.5
7	225 (4.88), 282 (3.85)	476, 510, 550	251.3 ± 0.5

analogues **4** and **5** are similar to the spectrum of a 1:1 (mol/mol) mixture of 3-phenyl-5-methylcyclopent-2-enone and ethylnaphthalene, suggesting no ground state interactions between the enone and naphthalene chromophores.

Emission spectroscopy

None of the compounds **1**–**5** is found to emit in fluid solution. In the cases of **4** and **5** this is consistent with efficient energy transfer between the naphthalene and the lower lying enone singlet states. The phosphorescence spectra of the cyclopentenone derivatives were recorded in ethanol–isopentane–diethyl ether (2:5:5, v/v) (EPA) at 77 K and those of **2**–**5** are shown in Fig. 1. For comparison the spectrum of 1-ethylnaphthalene **7**, which has been measured previously in diethyl ether–THF (1:1, v/v),[10] was also recorded in EPA (Fig. 1). Interestingly, its spectrum is very similar to that of the enones **1**–**5**, although different from that of naphthalene itself.[11] Triplet energy levels derived from the highest energy vibrational band peak in the phosphorescence spectrum for compounds **1**–**5** are given in Table 1. The similarity of the emission spectra of the enones **4** and **5** with the 1-substituted naphthalenes means that it is not possible to be sure whether the phosphorescence in **4** and **5** is originating in the enone or naphthyl moiety.

Phosphorescence lifetime measurements for compounds **1**, **2** and **3** in EPA and diethyl ether–ethanol (1:1, v/v) glasses could not be fitted to a single exponential. However satisfactory fitting to double exponential decays for these compounds was achieved. Varying the laser intensity (by 20-fold), concentration (by five-fold), monitoring wavelength, excitation wavelength and oxygen concentration did not affect the resulting decay kinetics. (By contrast benzophenone and 1-methylnaphthalene in EPA at 77 K exhibited single exponential traces with lifetimes comparable to literature values.)[12,13] However single exponential decays were recorded for compound **1** in either pure ethanol or in diethyl ether–tetrahydrofuran (1:1, v/v) glasses at 77 K and the lifetimes obtained (57 and 24 ms respectively) are close to those obtained for the two decays recorded in EPA (Table 2). The double exponential in EPA may therefore be assigned to solvent site effects, with molecules in non-polar ether regions exhibiting a lifetime of 23 ± 3 ms whereas those with alcohol neighbours are longer lived: 58 ± 6 ms. Similar behaviour is found for the compounds **2** and **3** (Table 2) although the lifetimes are somewhat longer. The ratio of the two components is also affected. It is observed that a greater proportion of the recorded phosphorescence arises from non-polar ether regions in the case of **2** and **3** compared to that of **1**. This is consistent with compound **1** being more polar than either of **2** or **3**.

By contrast the emission from the naphthyl-substituted enones **4** and **5** is more complex and even in ethanol single exponential behaviour is not observed. However the decay contains a component with a lifetime of *ca.* 65 ms (comparable to that found for compounds **1**, **2** and **3**) accompanied by a component with a lifetime of *ca.* 300 ms. This latter constituent could be due to emission from the enone excited state repopulated from the alkylnaphthalene localised state or possibly directly from the alkylnaphthalene itself.

Flash photolysis

The triplet state absorption spectra and lifetimes have been measured for compounds **1**–**5** in degassed cyclohexane solution at room temperature. The spectra of the triplet states of phenylalkyl compounds **2** and **3** show a broad band centred around 370 nm, shifted by about 10 nm from that of the unsubstituted enone **1** (Fig. 2).[5] The lifetimes of **2** and **3** are significantly shorter than **1**. As with that compound, there is quenching of the excited state by the ground state (Table 3). The rate constant for quenching by molecular oxygen of compound **3** was determined to be 1.6×10^9 dm^3 mol^{-1} s^{-1}.

The triplet state spectrum of the naphthylmethyl compound **4** (Fig. 2) in cyclohexane shows peaks at 370, 399 and 424 nm. The first is characteristic of an enone-centred triplet state while the longer wavelength peaks may be assigned to the naphthyl-centred triplet state by comparison with the triplet transient absorption spectrum for 1-ethylnaphthalene[14] (Fig. 2). The lifetime of **4** is 90 ns, significantly shorter than that of its phenylmethyl analogue **2**. This effect is also observed for the homologous phenylethyl and naphthylethyl compounds **3** and **5**; however the lifetime of **5** is somewhat longer at 500 ns. The rate constant for quenching by molecular oxygen for **5** is 1.7×10^9 dm^3 mol^{-1} s^{-1}. The spectrum of **5** shows similar features to that of **4** but the band at 399 nm is relatively more intense for **4** than for **5**. For both **4** and **5** the decay kinetics monitored at 370 nm [the enone (E) chromophore] or at 424 nm [the naphthalene (N) chromophore] are the same within experimental error. This is strongly indicative of equilibration between the two chromophores [eqn. (1)].

$$E\text{–}N^T \xrightleftharpoons{K_{eq}} E^T\text{–}N \qquad (1)$$

$$K_{eq} = [E^T\text{–}N]/[E\text{–}N^T] \qquad (2)$$

The equilibrium constant K_{eq} for **5** can therefore be determined from the relative absorbances (A) of the signals at 370 and 424 nm if the decadic molar absorption coefficients of the enone (ε_E) and naphthalene (ε_N) chromophores of **5** are known. These were determined by relative actinometry using naphthalene in cyclohexane as a reference (for details see the Experimental section).[14] From these values the equilibrium constant from eqn. (1) was calculated using the ratio of the concen-

Table 2 Time resolved emission data for enones **1**–**5** measured at 77 K[a]

Comp.	Solvent	$(A_1/A_1 + A_2)$ (%)	τ_1/ms	$(A_2/A_2 + A_1)$ (%)	τ_2/ms
1	Ethanol	100	57	—	—
	Ethanol–diethyl ether	65	57	35	23
	EPA	58	59	42	23
	Diethyl ether–THF	—		100	24
2	Ethanol	100	67	—	—
	EPA	43	69	57	25
3	Ethanol	100	72	—	—
	EPA	44	73	56	32
4[b]	Ethanol	90	65	10	300
5[b]	Ethanol	90	65	10	300

[a] Decay traces fitted to the expression $A_1\,e^{-t/\tau_1} + A_2\,e^{-t/\tau_2}$. [b] The data for **4** and **5** are approximate fits.

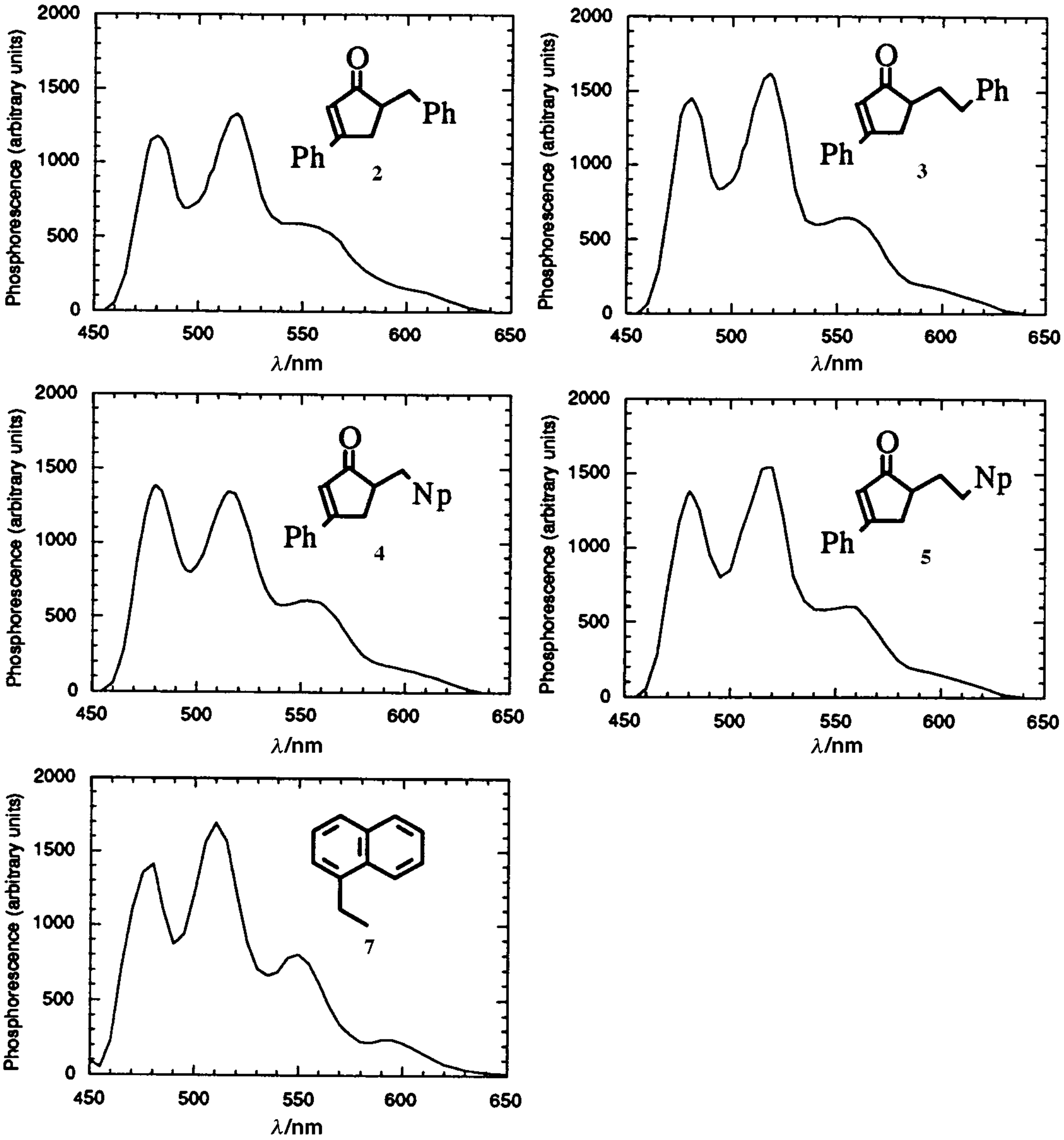


Fig. 1 Phosphorescence spectra of compounds **2**–**5** and of 1-ethylnaphthalene (**7**) recorded in EPA glasses at 77 K

trations evaluated for $(A_{E^T}/\varepsilon_{E^T}):(A_{N^T}/\varepsilon_{N^T})$, assuming that ε_{E^T} is the same in E^T–N as it is for the triplet state of **1** and that ε_{N^T} of E–N^T is the same as that of the triplet state of 1-ethylnaphthalene (Table 4). The determined ratio for [E^T–N] : [E–N^T] is given by (0.74 : 0.26) and leads to a value for K_{eq} of 2.9 and hence a calculated value for the free energy ($\Delta G°$) of -2.6 kJ mol^{-1} at 298 K in cyclohexane solution. This is comparable with the triplet energies obtained from the phosphorescence measurements in EPA at 77 K which give an enthalpy difference between the enone and alkylnaphthalene triplet states of -2.1 ± 1.0 kJ mol^{-1} (Table 1).

Discussion

The transient absorption and kinetic studies that we have performed allow us to probe the interaction of the enone and naphthalene moieties in their ground and excited state. The observations made can be explained in terms of the energy diagram in Fig. 3.

The absorption spectra of compounds **2**–**5** imply no intramolecular ground state interactions between the chromophores. However the bichromophorics will explore a number of geometries during the lifetime of the triplet state and a *gauche*

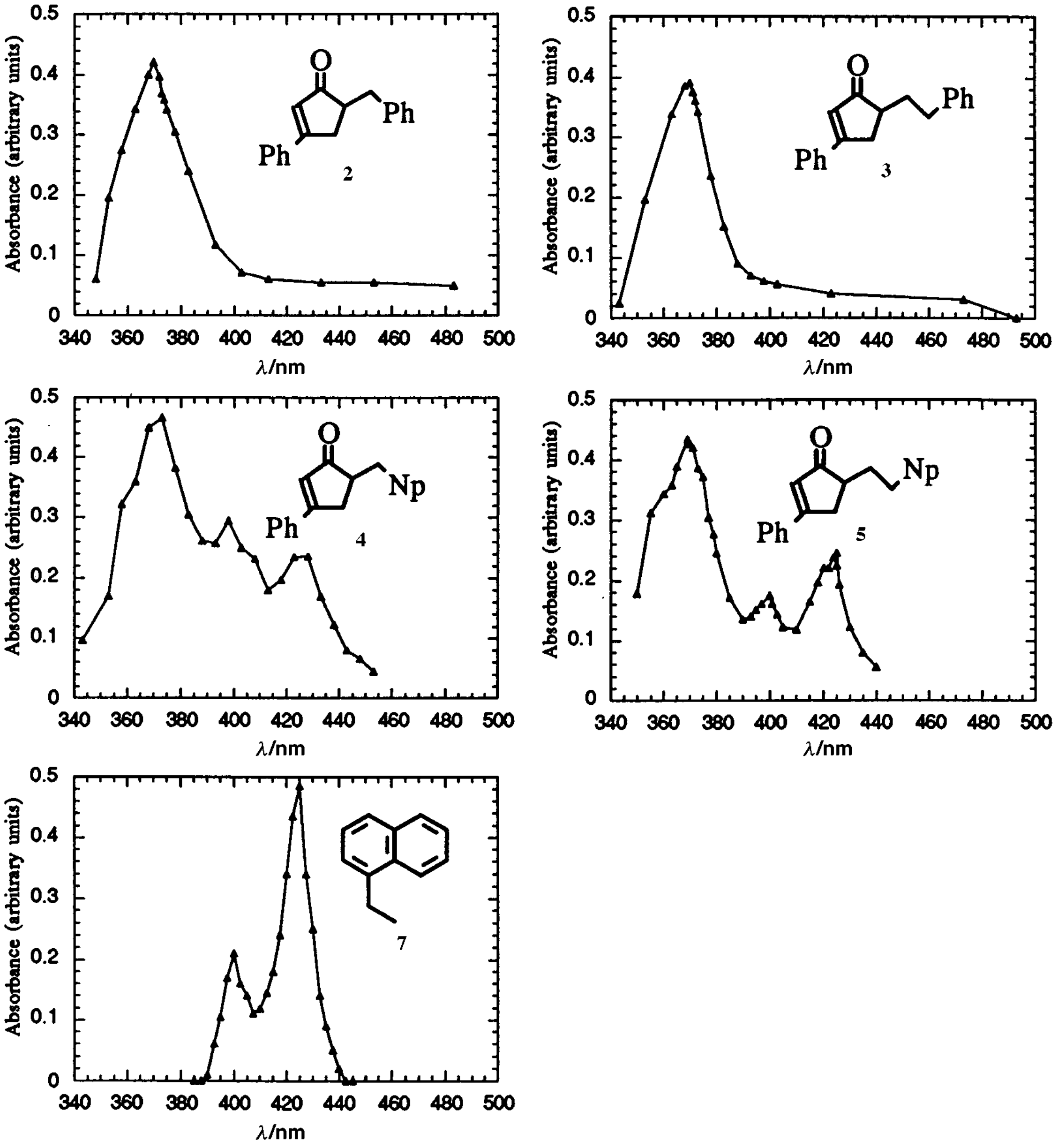


Fig. 2 The triplet state absorption spectra of compounds **2**–**5** and of 1-ethylnaphthalene (**7**) in cyclohexane at 298 K, observed following 308 nm laser excitation

Table 3 The triplet transient absorption bands and lifetime at infinite dilution (τ_0) for enones **1**–**5** and rate constants for self quenching for compounds **1**–**3**, in cyclohexane

Comp.	Principal bands/nm	τ_0/μs	k_{sq}/dm^3 mol^{-1} s^{-1}
1	360	24 ± 1	3.5 ± 0.5 × 10^8
2	370	8.1 ± 0.5	2.5 ± 0.5 × 10^8
3	369.5	14.2 ± 0.5	2.3 ± 0.5 × 10^8
4	370, 399, 424	0.09 ± 0.01	—
5	370, 399, 424	0.50 ± 0.05	—

Table 4 The absorbance of the triplet states and corresponding extinction coefficients[a] for enones **3**, **5** and ethylnaphthalene **7** in cyclohexane,[b] following laser excitation at 308 nm

Comp.	λ/nm	A_T	ε_T/dm^3 mol^{-1} cm^{-1}
1	360	0.213 ± 0.005	15 500
5 (E*)	370	0.197 ± 0.005	14 300
5 (N*)	424	0.103 ± 0.005	7 600
7	424	0.408 ± 0.005	22 000

[a] Determined using triplet state of naphthalene as standard actinometer. [b] All samples had ground state absorbances of ~0.30 at 308 nm.

conformation would allow for a closer proximity of the chromophores and thus facilitate interaction.

The absence of naphthalene fluorescence in **4** and **5** is indicative of energy transfer from the naphthalene singlet state to the low lying ^{1}(n–π*) state of the enone. There are quite a few examples from the literature of such energy transfers occurring intramolecularly from the naphthyl chromophore to chromophores linked either by flexible methylene chains[13,15,16] of varying length or by rigid spiro linkages.[17,18] This singlet–singlet energy transfer process is competitive with intersystem crossing of the naphthalene singlet state to the triplet state and the fluorescence decay process of the naphthalene chromophore. No emission is observed from the enone ^{1}(n–π*) state. The ^{1}(n–π*)→S_0 transition is an orbital overlap and orbital symmetry forbidden process, consequently enones are expected to fluoresce very weakly. In contrast the process of intersystem crossing for cyclopentenones and cyclohexenones should be rapid.

The photophysical characteristics of **2** and **3** are closely similar to those of the parent enone **1**. The lower self quenching rate constants relative to **1** may be related to the steric hin-

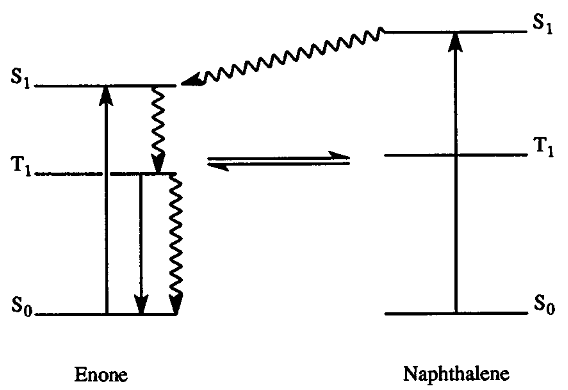
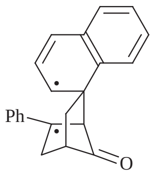


Fig. 3 Pathway following excitation of the naphthyl-substituted enones **4** and **5**

drance imposed by the phenylalkyl substituent hindering intermolecular interactions. It is known that the phenylmethyl derivative **2** forms cyclobutane dimers.[7] It is also probable that the phenylalkyl substituents increase the total degree of molecular motion in the entire molecule and thus shorten the lifetime of the triplet states of **2** and **3** relative to **1**.

A similar effect would be expected for the naphthyl-substituted compounds. However the lifetime of the enone triplet is considerably shorter in the naphthyl bichromophorics **4** and **5** than in the phenyl analogues **2** and **3** indicating that there is an additional process in competition with the non-radiative decay process for the former compounds. Both compounds **4** and **5** are known to undergo intramolecular photochemical processes. In the case of the naphthylmethyl **4** compound cyclobutane formation is observed.[7] In the case of the naphthylethyl **5** compound, γ-hydrogen abstraction is apparently preferred to cyclobutane formation, with low yields of 1-vinylnaphthalene **11** being detected.[19] In each case biradical intermediates can be postulated, **8** in the transformation of **4** to the cyclobutane **9**, and **10** in the transformation of **5** to 1-vinylnaphthalene **11** and the parent enone **1**. It is possible that the shorter lifetimes of **4** and **5** are due to the formation of very short lived biradical species of this type.



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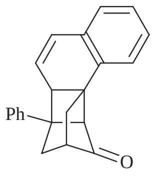

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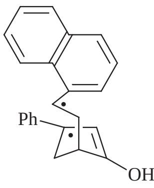

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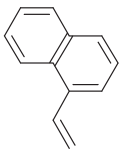

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No intramolecular excited state energy transfer is expected between the phenyl group and the enone, as the singlet ($E_S = 459$ kJ mol^{-1}) and triplet ($E_T = 353$ kJ mol^{-1}) energies[12] of the phenyl group are too high to be accessible. However such triplet–triplet energy transfer is found for the naphthyl compounds **4** and **5** as the energies of the enone and naphthyl-centred excited states lie close together (Table 1). Due to this and the relatively long lifetime of both the enone and naphthalene triplet states in solution compared to the rate of triplet–triplet energy transfer, direct observation of the equilibrium between the two triplet states should be possible (Fig. 3). That this does indeed occur is demonstrated by our observation of absorbance bands corresponding to both enone and naphthalene centred triplet states, both of which decay at the same rate. This reversible triplet–triplet energy transfer is presumably occurring *via* an exchange mechanism. As in previous cases[15] we believe that the alkyl chain does not directly participate in energy transfer. It is more probable that the ethylene link provides greater flexibility to achieve a conformation favouring energy transfer.

Given the lifetime of the naphthyl chromophore (in cyclohexane solution) it is most likely that the triplet manifold of **4** or **5** is decaying to the ground state *via* the enone triplet. The only other case of intramolecular reversible triplet energy transfer of which we are aware is that reported by Wagner and Nakahira.[20] They measured temperature effects on the ratio of products formed by γ-hydrogen abstraction (from the connecting methylene chain) by the benzoyl group or the anisoyl group of 1-benzoyl-4-(4-anisoyl)butane and found that the product ratio is independent of the excitation wavelength and decreases with increasing temperature. They rationalise these results in terms of a reversible internal conversion of the n–π* state of the benzoyl group ($E_T = 301$ kJ mol^{-1}) and the π–π* state of the anisoyl group ($E_T = 279$ kJ mol^{-1}).

Complex emission decay

Each of the enones **1**–**3** shows double exponential decays in EPA which appears to be explained by a solvent site effect as single exponential behaviour is found in either pure ethanol or mixed diethyl ether–THF glasses. The dominant component of the double exponential decay for 3-phenylcyclopentenone in EPA glass at 77 K exhibits a lifetime of 57 ms, similar to that of 53 ms previously reported by Magnifico *et al.*[21] Non-exponential decay, of acetophenone and indan-1-ones, has previously been attributed to the existence of metastable states.[22,23] For the case of indan-1-ones[24] the longer lived emission arises from molecules hydrogen bonded to the solvent and the short lived emission from molecules in a non-protic solvent cage, in agreement with solvent effects on mixing of close-lying n–π* and π–π* states. It has been shown[25] that both states exist for constrained enone steroid systems and that they lie very close together in energy.

Similar effects should be observed in the naphthyl substituted enones **4** and **5** but the decay is complicated by the longer lived emission of either the alkylnaphthalene triplet state or repopulation of the enone from this state. Back energy transfer is not expected to occur as effectively in rigid glasses as in solution as the molecular motion is restricted, therefore the molecules cannot readily achieve an orientation suitable for energy transfer.

Experimental

Photophysical measurements

Materials. 3-Phenylcyclopent-2-enone was prepared according to the literature.[26] 1-Ethylnaphthalene was supplied by Aldrich. Cyclohexane (BDH Spectrosol grade) was used. Diethyl ether was distilled over sodium–benzophenone. Isopentane (Aldrich spectroscopic grade), 96% ethanol (Merck) and tetrahydrofuran (Riedel de Haen Chromosol™ grade) were used without further purification.

Instrumentation. The specifications of the flash photolysis are as outlined in Kelly *et al.*[27] Briefly, it consists of a Lambda Physik EMG-50 XeCl excimer laser emitting at 308 nm (pulse width *ca.* 15 ns, pulse energy 20 mJ). All solution concentrations were chosen with an absorbance of less than 0.8 at 308 nm, and degassed by three freeze–pump–thaw cycles.

Determination of the decadic molar absorption coefficients of the triplet states of ethylnaphthalene, the parent enone and the chromophores were calculated from the excited state absorbance of the species (A_T) compared to (A_R) of naphthalene for which $\varepsilon_R = 24{,}500$ dm^3 mol^{-1} cm^{-1} and the quantum yield of intersystem crossing $\Phi_R = 0.80$. For these experiments the ground state absorbance of the reference and sample solutions were all similar (about 0.30). The extinction coefficient of the transient under investigation (ε_T) was determined using eqn. (3).

$$\varepsilon_T = [(A_T \times \Phi_R)/(A_R \times \Phi_T)]\varepsilon_R \qquad (3)$$

Phosphorescence spectra were recorded using a Perkin-Elmer

MPF-44B spectrofluorimeter, with a 150 W Xenon lamp as the light source and Hamamatsu R928 red-sensitive photomultiplier. The spectra were recorded on a Gow Mac 70–700 printer and subsequently digitised at intervals of 2 to 5 nm. Low temperature conditions were achieved using an Oxford Instruments DN704 liquid nitrogen cryostat with the sample dissolved in ethanol–isopentane–diethyl ether (2:5:5 v/v) in a 2 mm quartz cuvette.

Phosphorescence decays monitored at 520 nm were recorded using a Tektronix TDS-380 digital oscilloscope following excitation with a Lambda Physik EMG-50 XeCl excimer laser. Additionally, excitation wavelength variation was achieved using an Edinburgh Instruments single photon counting (SPC) Fl-900 spectrometer μF-900 flashlamp. Decays observed by both techniques are similar. Samples were placed in a quartz tube (3 mm diameter), in an Oxford instruments DN-704 cryostat cooled to 77 K.

Synthesis

Materials and methods. For general procedures see Part 6.[7] Tetrahydrofuran (GPR grade) was dried over calcium chloride, distilled from lithium aluminium hydride and finally distilled from sodium–benzophenone before use. The IR spectra of liquids were measured as films, and those of solids as Nujol mulls. IR data were recorded in wavenumbers. ^{1}H NMR spectra were measured on either a Bruker WP80 (80 MHz) or MSL 300 (300 MHz) instrument as solutions in deuteriochloroform unless otherwise stated. NMR data are recorded in δ values and coupling constants are in Hz. ^{13}C NMR spectra were recorded on a Bruker MSL300 instrument (75.5 MHz). Melting points were determined on a Griffin melting point apparatus and are uncorrected.

Procedure. The preparation of **2** has been described previously.[7]

Ethyl 2-*acetyl*-4-*phenylbutanoate* (**12**).—Ethyl 3-oxobutanoate (26 g, 200 mmol) was added slowly to a stirred suspension of sodium hydride (4.8 g, 200 mmol) in tetrahydrofuran (100 cm^3) and the mixture stirred for 30 min. 1-Bromo-2-phenylethane (37 g, 200 mmol) was added and the reaction mixture stirred at 60 °C for 24 h. The mixture was poured into water, and this was extracted with diethyl ether (3 × 60 cm^3). The combined diethyl ether layers were washed with water and dried (MgSO$_4$). The solvent was removed to afford the keto-ester as an oil which was fractionally distilled (bp 100 °C, 0.3 mbar), (5.6 g, 12%); ν_{max} 1734, 1714; δ_H 1.27 (t, J 7.1, 3H), 2.10 (m, 2H), 2.17 (s, 3H), 2.60 (m, 2H), 3.14 (t, J 7.2, 1H), 4.20 (q, J 7.1, 2H) and 7.20–7.28 (m, 5H).

Ethyl 2-*acetyl*-2-(2-*phenylethyl*)-4-*oxo*-4-*phenylbutanoate* (**13**).—The above keto-ester (5.6 g, 24 mmol) was added dropwise to a suspension of sodium hydride (0.58 g, 24 mmol) in tetrahydrofuran (30 cm^3). Sodium iodide (100 mg) was added, followed by phenacyl bromide (4.8 g, 24 mmol). The mixture was refluxed for 16 h, cooled and poured into water. The aqueous solution was extracted with diethyl ether (3 × 50 cm^3) and the combined ether layers dried (MgSO$_4$). Removal of the solvent gave the diketo-ester (7.36 g, 87%); ν_{max} 1727, 1705, 1683; δ_H 1.25 (t, J 7.1, 3H), 2.10 (m, 2H), 2.20 (s, 3H), 2.40 (s, 2H), 2.50 (m, 2H), 4.22 (q, J 7.1, 2H) and 7.16–8.02 (m, 10H).

3-*Phenyl*-5-(2-*phenylethyl*)*cyclopent*-2-*enone* (**3**).—The above diketo-ester (4.73 g, 13.5 mmol) and potassium hydroxide solution (500 cm^3, 1% in water–ethanol, 5:1) were heated at 85 °C for 2 h. The solution was cooled and solid potassium hydroxide (50 g) was added to bring up the concentration to 10%, and the mixture refluxed for a further 2 h. The mixture was cooled, and extracted with chloroform (4 × 50 cm^3). The combined chloroform layers were dried (MgSO$_4$). Removal of the solvent followed by flash chromatography (ethyl acetate–hexane, 1:6) and sublimation (90 °C at 4×10^{-2} mbar) afforded the *cyclopentenone* **3** (1.2 g, 34%); mp 67–69 °C (Found: C, 86.62; H, 7.06. $C_{19}H_{18}O$ requires C, 86.99; H, 6.92%); ν_{max} 1688, 1601; δ_H(Bruker DPX 400) 1.76 (ddt, J 13.8, 5.7, 9.2, 1H), 2.24 (dddd, J 13.8, 9.4, 7.0, 4.6, 1H), 2.58 (dddd, J 7.0, 5.9, 4.6, 2.6, 1H), 2.77 (m, 3H), 3.23 (ddd, J 18.3, 6.9, 1.74, 1H), 6.55 (t, J 1.74, 1H), 7.1–7.8 (m, 10H). In [^{2}H$_6$]DMSO the multiplet at 2.77 separates into a double triplet at 2.84 (J 18.3, 2.0, 1H) and a multiplet at 2.72 (2H); δ_C 33.3 (t), 33.5 (t), 35.4 (t), 45.5 (d), 126.0 (d), 126.7 (d), 126.8 (d), 128.4 (d), 128.5 (d), 128.9 (d), 131.2 (s), 134.0 (s), 141.2 (s), 172.2 (s) and 211.0 (s).

Ethyl 2-*acetyl*-(1-*naphthyl*)*butanoate* (**14**).—Ethyl 3-oxobutanoate (2.44 g, 19 mmol) in dimethoxyethane (20 cm^3) was added slowly to a suspension of sodium hydride (740 mg, 18.5 mmol) in dimethoxyethane (7 cm^3) at 5 °C and under a nitrogen atmosphere. 1-Bromo-2-(1-naphthyl)ethane **15**[28] (4.0 g, 17 mmol) in dimethoxyethane (30 cm^3) was added dropwise, the cooling bath removed and the reaction mixture stirred at 60 °C for 16 h. Sodium chloride solution (10%) (100 cm^3) was added, and the product extracted with diethyl ether (3 × 30 cm^3). The organic layers were washed with water and dried (MgSO$_4$). After removal of solvent and unreacted ethyl 3-oxobutanoate the residue was purified by flash chromatography (ethyl acetate–hexane, 1:9) to give the keto-ester as an oil (2.09 g, 43%); ν_{max} 1710 and 1735; δ_H 1.21 (t, J 8.9, 3H), 2.14 (s, 3H), 2.30 (m, 2H), 3.05 (m, 2H), 3.39 (t, J 8.8, 1H), 4.15 (q, J 8.9, 2H), 7.26–7.85 (m, 7H).

Ethyl 2-*acetyl*-2-[2-(1-*naphthyl*)*ethyl*]-4-*oxo*-4-*phenylbutanoate* (**16**).—Ethyl 2-acetyl-4-(1-naphthyl)butanoate (7 g, 24 mmol) in dimethylformamide (100 cm^3) was added slowly to a suspension of sodium hydride (1.2 g, 30 mmol) in dimethylformamide (30 cm^3) under an atmosphere of nitrogen, and the mixture stirred for 20 min. Phenacyl bromide (4.9 g, 25 mmol) in dimethylformamide (120 cm^3) was added dropwise, and the mixture was stirred at 70 °C for 4 h, cooled and poured into water. The solution was extracted with diethyl ether (3 × 40 cm^3), and the combined organic layers washed with water and dried (MgSO$_4$). Removal of the diethyl ether and dimethylformamide *in vacuo* left a residual oil, (7.14 g, 72%) which could be purified by flash chromatography (ethyl acetate–hexane, 1:5); ν_{max} 1735, 1705, 1685; δ_H 1.25 (t, J 8.8, 3H), 2.41 (s, 3H), 2.45 (m, 2H), 3.01 (m, 2H), 3.83 (s, 2H), 4.22 (q, J 8.8, 2H), 7.25–8.12 (m, 12H).

5-[2-(1-*Naphthyl*)*ethyl*]-3-*phenylcyclopent*-2-*enone* (**5**).—Ethyl 2-acetyl-2-[2-(1-naphthyl)ethyl]-4-oxo-4-phenylbutanoate (1.0 g, 2.5 mmol) in ethanol (30 cm^3), and sodium hydroxide solution (1%, 50 cm^3) were stirred for 48 h at room temperature. The reaction was monitored by following the disappearance of the carboxy absorption (IR). The mixture was neutralised with dilute sulfuric acid, and extracted with diethyl ether (3 × 40 cm^3). The diethyl ether layer was washed with sodium chloride solution (10%) and dried (MgSO$_4$). Removal of the diethyl ether afforded 5-(1-naphthyl)-3-acetyl-1-phenylpentan-1-one (670 mg, 81%), ν_{max} 1705 and 1685.

This diketone (670 mg) in benzene (15 cm^3) was added dropwise to a suspension of sodium hydride (100 mg, 2.5 mmol) in benzene (5 cm^3) under nitrogen. The mixture was refluxed for 1 h, and cooled. Water (50 cm^3) was added cautiously, and the aqueous layer extracted with diethyl ether. The organic layer was dried (MgSO$_4$). Removal of the solvent and flash chromatography (ethyl acetate–hexane, 1:6) of the residue gave the *cyclopentenone* **5** (312 mg, 40%), mp 102–103 °C (Found: C, 88.88; H, 6.69. $C_{23}H_{20}O$ requires C, 88.42; H, 6.45%); λ_{max}(cyclohexane)/nm 272 (log ε 4.48); ν_{max} 1690; δ_H 1.76–2.86 (m), 3.14–3.44 (m), 6.55 (t, J 2.1, 1H), 7.13–8.13 (m).

5-(1-*Naphthylmethyl*)-3-*phenylcyclopent*-2-*enone* (**4**).—To a solution of 1-(chloromethyl)naphthalene (1.77 g, 10 mmol) was added 1,8-diazabicylo[5.4.0]undec-7-ene (1.68 g; 11 mmol) and the enone ester **6**[8,29] (2.20 g, 10.2 mmol) in dry xylene (10 cm^3). The mixture was stirred for 16 h at room temperature. To the resulting brown mixture water was added and the organic phase was collected. Drying (Phase-Sep^{TM} paper), followed by removal of the solvent gave a brown oil. This was dissolved in tetrahydrofuran (25 cm^3). Aqueous 2.5 M sodium hydroxide (5 cm^3), water (5 cm^3), methanol (10 cm^3), and sodium methoxide (0.1 g) were added and the mixture was stirred for a further 16 h at room temperature. This was then diluted with aqueous sodium chloride (300 cm^3) and extracted with ethyl acetate (4 × 50 cm^3). The combined organic extracts were washed with brine, dried (Phase-Sep paper), and the solvent was removed to give a brown oil (2.72 g). This was purified by flash chromatography (ethyl acetate–hexane, 3 : 7) to give an almost colourless solid which was recrystallised from ethyl acetate–hexane to give small colourless needles (1.04 g; 35 %); mp 124–125 °C and mixed mp (127–128 °C).[7]

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