The Photochemistry of α-Arylcarboxylic Anhydrides. Part 3.[1,2] Photoreactions and Luminescence Spectra of 1- and 2-Naphthylacetic Anhydrides and 1,3-Di-(1-naphthyl)propan-2-one

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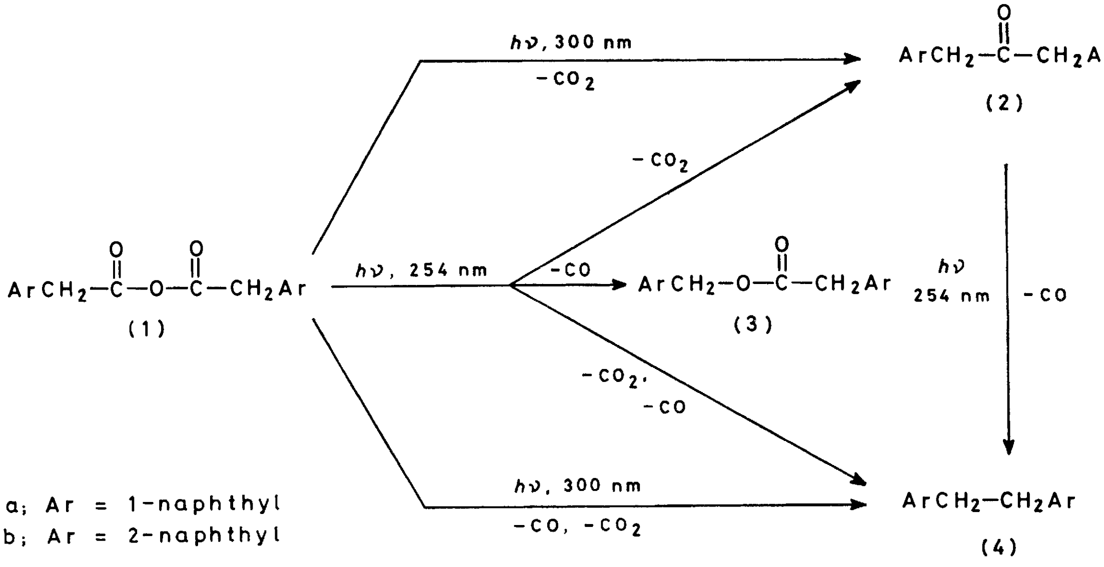
The photochemistry of 1- and 2-naphthylacetic anhydride and the luminescence of these anhydrides and of two naphthyl-substituted propanones has been studied. 1-Naphthylacetic anhydride upon irradiation with λ 300 nm yields mainly 1,3-di-(1-naphthyl)propan-2-one. With λ 254 nm, the main product is 1,2-di-(1-naphthyl)ethane. 1,3-Di-(1-naphthyl)propan-2-one proved to be photostable for λ 300 nm; it is, however, photoreactive upon irradiation with λ 254 nm and then yields 1,2-di-(1-naphthyl)ethane. Essentially similar results have been obtained with 2-naphthylacetic anhydride. With both anhydrides a characteristic emission at λ *ca.* 400 nm has been observed which is ascribed to intramolecular excimer fluorescence. The excimer emission is more pronounced with the naphthylacetic anhydrides (with 6 σ bonds between the two naphthyl groups) than with 1,3-di-(1-naphthyl)propan-2-one (with 4 σ bonds between them). The assignment of the emission of the ketone at λ 400 nm to excimer fluorescence was made on the basis of a comparison with 1-(1-naphthyl)propan-2-one, which cannot form an intramolecular naphthyl excimer. Molecular model studies suggest that both the anhydrides and 1,3-di-(1-naphthyl)propan-2-one can adopt a sandwich type of conformation required for intramolecular excimer formation. The absence of fluorescence of the naphthalene monomer type for 1,3-di-(1-naphthyl)propan-2-one as well as its photostability (λ 300 nm) may be explained in terms of intramolecular transfer of singlet energy from the naphthyl to the carbonyl group, followed by intersystem crossing and subsequent intramolecular quenching of the carbonyl triplet by the naphthyl moiety.

In a previous study, dealing with the photochemistry of phenylacetic acids and anhydrides, it was observed that irradiation of these substrates at λ 254 nm leads to bibenzyls as the main product.[1] With *o*- and *p*-methoxyphenylacetic anhydrides, however, substantial amounts of ester, *i.e.* the corresponding methoxybenzyl methoxyphenylacetate, were produced additionally. It was proposed that the formation of the bibenzyl occurs by a recombination of radicals resulting from a Norrish Type I reaction of the anhydride, but that the ester was formed *via* a dipolar intermediate.

In order to obtain information on the effect of lowering the excited state energies of the aryl moiety, we have now investigated the photochemistry of the corresponding 1- and 2-naphthylacetic anhydrides with both λ 300 and 254 nm. In order to obtain a more complete picture of the possible modes of decay of the excited states, the luminescence of these anhydrides and of some related propanones was also studied.

RESULTS AND DISCUSSION

Photoreactions.—Irradiation of the naphthylacetic anhydrides (1) in acetonitrile with λ 300 nm resulted in the formation of (2) and (4), some CO, CO_2, polymeric material, and in the case of (1b) traces of (3b) (see Scheme 1 and Table). Upon irradiation of (1a), (3a) is not formed beyond the limit of detection, which is *ca.* 1%. The formation of large amounts of (2) compared with (4) may indicate that the formation of (2) proceeds mainly from the excited carboxylic anhydride, by either a



Scheme 1

Photoreactions of the two symmetrical naphthylacetic anhydrides (1) and 1,3-di-(1-naphthyl)propan-2-one (2a) [a]

Substrate	Substrate concentration (mM)	λ/nm	Irradiation time (h)	Substrate conversion (%)	Product [b] (%)
(1a)	10	254	5	90	(2a) (32), (3a) (5), (4a) (50)
(1a)	30	300	50	15	(2a) (8), (4a) (<1), polymer
(1b)	40	254	5	47	(2b) (24), (3b) (2), (4b) (18)
(1b)	40	300	22	25	(2b) (15), (3b) (<1), (4b) (6)
(2a)	160	254	5 [c]	33	(4a) (30)
(2a)	160	300	16 [c]	*d*	*d*

[a] In acetonitrile as solvent; Rayonet photochemical reactor, 32°. [b] Conversion of substrate and yield of products determined by ^{1}H n.m.r. [c] In CD_3CN. [d] No photoreaction was observed.

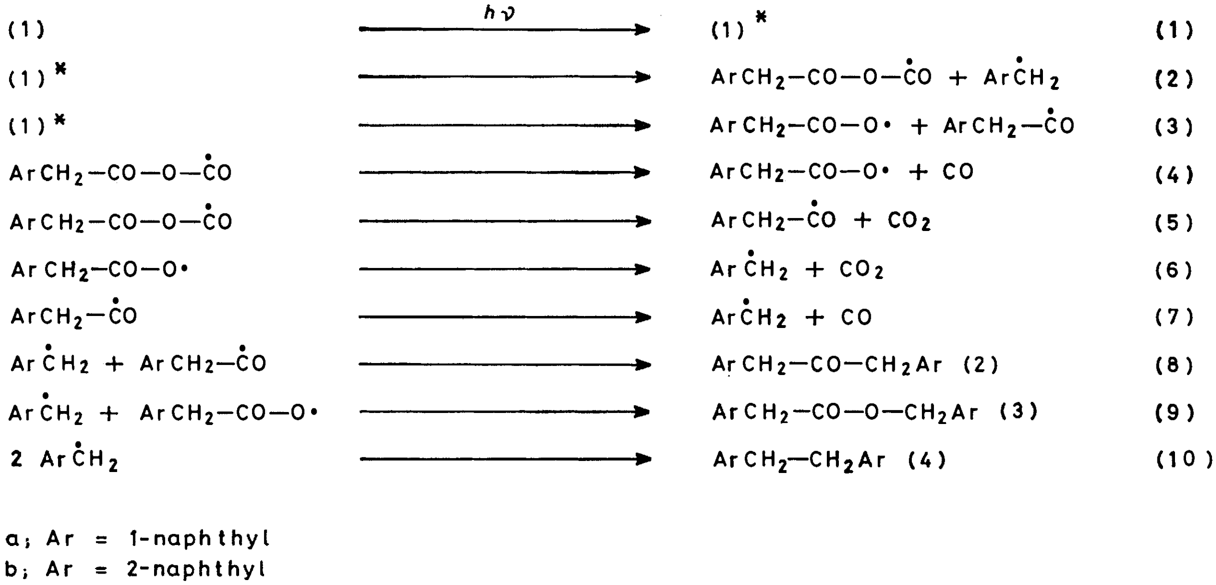
concerted loss of CO_2 or an efficient cage recombination, since bimolecular reaction of free naphthylacetyl radicals [to give *e.g.* (2)] prior to decarbonylation seems improbable.

The ketone (2a) is photostable at λ 300 nm. The behaviour of this ketone contrasts sharply with that of the phenyl analogue, 1,3-diphenylpropan-2-one, which upon irradiation at λ 300 nm decarbonylates, yielding bibenzyl, with a quantum efficiency of 0.7.[3] The ester (3b) is reported to yield (4b) upon irradiation at λ 300 nm.[4]

The main product upon irradiation of (1a) at λ 254 nm is (4a); smaller amounts of the ketone (2a) and the ester (3a) are formed (see Scheme 1 and Table). For this wavelength the ketone (2a) is not photostable and affords substantial amounts of (4a). The formation of (4a) upon irradiation of (1a) possibly originates in part from a photoreaction of initially produced (2a). Irradiation of (1b) with λ 254 nm affords substantial amounts of (2b) along with smaller amounts of the bibenzyl (4b) and traces of the ester (3b).

The formation of the various products (2)—(4) upon irradiation of the naphthylacetic anhydrides may be explained by the radical mechanism outlined in Scheme 2. The initial step in this mechanism involves homolytic cleavage at either side of one of the carbonyl groups of the anhydride (steps 2 and 3). Combination of two naphthylmethyl radicals (formed by steps 2, 6 and/or 7), combination of a naphthylacetyl radical (formed by steps 3 and/or 5) and a naphthylmethyl radical, and combination of a naphthylacetoxyl radical (formed by step 3) with a naphthylmethyl radical then account for the formation of the products (4), (2), and (3), respectively. The fact that only small amounts of the esters (3) were found renders it difficult to assess any contribution of an ionic type of mechanism for the formation of (3), as was established for the ester formation in the photolysis of a series of *o*- and *p*-methoxy-substituted phenylacetic anhydrides.[1]

The observation that the ketone (2a) is photostable towards λ = 300 nm poses an interesting question as to the possibility of intramolecular sensitization and quenching, a phenomenon described by Lamola and co-workers.[5] Robbins and Eastman studied the photodecarbonylation of a number of substituted 1,3-diphenylpropan-2-ones.[3] They discovered that upon *p*-cyano substitution, the photodecarbonylation is suppressed completely, which they explained in terms of intramolecular quenching. The very short-lived carbonyl triplets which undergo an efficient CO-photoelimination in the case of the unsubstituted 1,3-diphenyl-, 1,3-di-(*p*-tolyl)- and 1,3-di-(*p*-methoxyphenyl)propan-2-one (all with $\Phi = 0.7$) have a triplet energy of *ca.* 78 kcal mol^{-1} and may therefore be deactivated by the *p*-cyanophenylene group with $E_T = 77$ kcal mol^{-1}, but not



$$(1) \xrightarrow{h\nu} (1)^* \quad (1)$$

$$(1)^* \longrightarrow ArCH_2{-}CO{-}O{-}\dot{C}O + Ar\dot{C}H_2 \quad (2)$$

$$(1)^* \longrightarrow ArCH_2{-}CO{-}O\bullet + ArCH_2{-}\dot{C}O \quad (3)$$

$$ArCH_2{-}CO{-}O{-}\dot{C}O \longrightarrow ArCH_2{-}CO{-}O\bullet + CO \quad (4)$$

$$ArCH_2{-}CO{-}O{-}\dot{C}O \longrightarrow ArCH_2{-}\dot{C}O + CO_2 \quad (5)$$

$$ArCH_2{-}CO{-}O\bullet \longrightarrow Ar\dot{C}H_2 + CO_2 \quad (6)$$

$$ArCH_2{-}\dot{C}O \longrightarrow Ar\dot{C}H_2 + CO \quad (7)$$

$$Ar\dot{C}H_2 + ArCH_2{-}\dot{C}O \longrightarrow ArCH_2{-}CO{-}CH_2Ar\ (2) \quad (8)$$

$$Ar\dot{C}H_2 + ArCH_2{-}CO{-}O\bullet \longrightarrow ArCH_2{-}CO{-}O{-}CH_2Ar\ (3) \quad (9)$$

$$2\ Ar\dot{C}H_2 \longrightarrow ArCH_2{-}CH_2Ar\ (4) \quad (10)$$

a; Ar = 1-naphthyl
b; Ar = 2-naphthyl

SCHEME 2

by the phenyl group ($E_T = 84$ kcal mol^{-1}) or the *p*-methoxyphenylene group ($E_T = 81$ kcal mol^{-1}).[3,*]

A similar deactivating mechanism might be operative in the case of (2a), where the energy differences are probably even more advantageous for such a deactivation than with 1,3-bis-(*p*-cyanophenyl)propan-2-one. The suggested energy diagram for (2a) is drawn in Scheme 3. 1-Methylnaphthalene not only acts as a singlet sensitizer for ketones, it also quenches the triplet excited states of these compounds generated from the singlet excited state by intersystem crossing.[6] Schaffner invoked an intramolecular singlet sensitization of some 1-naphthylacetaldehydes by the naphthyl group to explain the observed photodecarbonylation of the aldehydes.[7] Considering the absorption characteristics of the carbonyl and 1-methylnaphthalene portions of (2a), all the radiation will be absorbed by the naphthyl chromophore, and it is thought that subsequently a very efficient *intramolecular* transfer of singlet energy to the ketone moiety will take place. The singlet excited ketone, in turn, will undergo a facile intersystem crossing ($\Phi > 0.8$),[8] and the resulting triplet excited ketone will be quenched intramolecularly very efficiently by the naphthyl chromophore.

The observation that the ketone (2a) does show photoreactivity upon irradiation at λ 254 nm can be explained by a facilitated bond homolysis of (2a) from an upper vibrational level of the excited naphthyl part of the ketone. A similar effect of wavelength of excitation on the reactivity has been observed in the photolyses of 1-(1-naphthyl)propan-2-one at λ 254 and 300 nm.†

Luminescence Spectra.—Naphthylacetic anhydrides. The room-temperature luminescence spectra of 1- and 2-naphthylacetic anhydride and the corresponding methylnaphthalenes are displayed in Figures 1 and 2, respectively. The intensity of the luminescence is given in arbitrary units and has not been corrected. However, in order to obtain a proper comparison of the luminescence spectra within a series of related compounds, the measurements have been performed on solutions of equal optical density for the wavelength of excitation. Upon decreasing the concentrations of the anhydrides by a factor of two, the emission signal reduces also by a factor of two. This indicates that the emission is not the result of an intermolecular process involving two naphthalene groups of unlike molecules. Further, upon excitation of the samples with different wavelengths (254 and 313 nm) essentially the same emission spectra are produced, rendering the presence of fluorescing impurities highly unlikely.

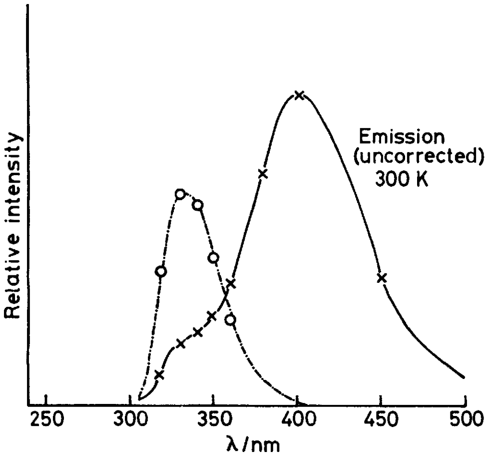


FIGURE 1 Emission spectra of 1-methylnaphthalene (— · — · — ·) and 1-naphthylacetic anhydride (———) in cyclohexane. Excitation wavelength 254 nm

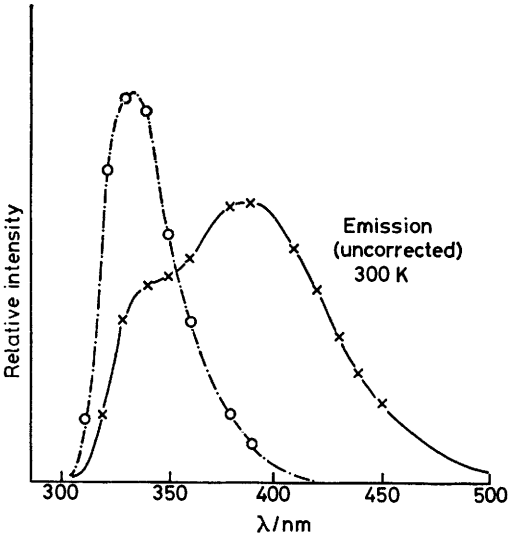


FIGURE 2 Emission spectra of 2-methylnaphthalene (— · — · — ·) and 2-naphthylacetic anhydride (———) in cyclohexane. Excitation wavelength 287 nm

The fluorescence of the two methylnaphthalenes at λ *ca.* 340 nm is exclusively of the monomer type.[9] With the anhydrides, by contrast, in addition to some residual (monomer) fluorescence at λ 340 nm, an emission centred at λ *ca.* 400 nm is observed, which is intramolecular in origin and which is likely to originate from the intramolecular excimer. This emission resembles the excimer fluorescence observed with systems containing two naphthyl chromophores.[10,11] Chandross *et al.* investigated a series of αω-di-(1-naphthyl)- and αω-di-(2-naphthyl)-alkanes and observed a maximum intensity of the excimer fluorescence for αω-dinaphthylalkanes with 4 σ bonds between the chromophores.[10,11] This is in accord with Hirayama's rule, which states that excimer fluorescence is to be found only when the two aromatic nuclei are connected by a trimethylene chain.[12] With 5 σ bonds between the chromophores there is hardly any indication of the presence of a sandwich dimer (excimer).[10,11]

With respect to the spatial arrangement of the anhydrides, the planar conformations (I)—(III) of the anhydride group may be considered. If the naphthyl rings were directly attached to the carbonyl groups, a perfect sandwich-type conformation would be attainable

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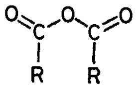
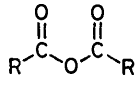
[*] The intramolecular energy transfer infers quenching of one state and the population of another (sensitization), and is a special case of internal conversion.

† J. A. J. Geenevasen, personal communication.

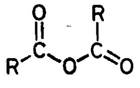
on the basis of anhydride conformation (I). This conformation is similar to the sandwich form proposed for 1,3-diphenyl- and 1,3-di-(1-naphthyl)propane in which



(I)



(II)



(III)

the aryl rings can be easily positioned parallel face to face, *ca.* 3 Å apart, which is in fact the required spatial arrangement for excimer formation.[10,12]

With the interposition of the methylene groups between the carbonyl and naphthyl groups, however, conformation (I) becomes unlikely, due to unfavourable steric interactions between these two methylene groups. For aliphatic anhydrides this conformation was also considered unlikely for the same reason.[13]

Conformation (II) can be ruled out *a priori*, as it gives rise to strong intramolecular repulsions between the two carbonyl dipoles. The spatial arrangement shows some resemblance to that of a pentamethylene chain, if the alkylene chain is assumed to take an extended *trans*-form. In the case of 1,5-di-(1-naphthyl)pentane a proper sandwich conformation can be achieved only with an internuclear distance of 4.5—5 Å.

In the case of the naphthylacetic anhydrides a conformation related to (II) is conceivable, but with a larger dihedral angle between the two carbonyl groups, as found for acetic anhydride and chloroacetic anhydride.[14,15] In our case, however, such conformations do not allow the naphthyl rings to approach each other any closer than is achievable for the dinaphthylalkanes with a pentamethylene chain, *i.e.* 4.5—5 Å. Finally, in (III) or related, slightly deformed planar conformations the naphthyl rings can indeed be positioned parallel to and on top of each other at a distance of 3—3.5 Å, as shown by a study of molecular models. The two conformations for the naphthylacetic anhydrides which allow excimer formation are shown schematically in Figure 3.

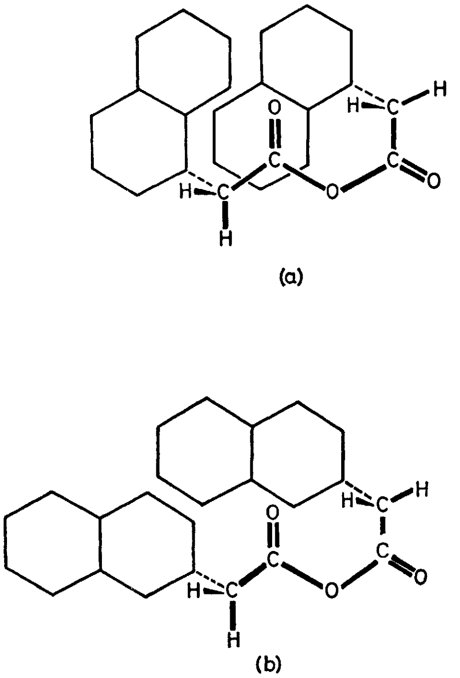


FIGURE 3 Conformations of 1-naphthylacetic (a) and 2-naphthylacetic anhydride (b). The anhydride function is situated in the plane of the drawing

The outcome of several studies [10,12,16] strongly suggests that some type of close, parallel arrangement of two aromatic rings is required for excimer formation. From consideration of the possible conformations we then conclude that excimer formation is feasible for the anhydrides under study and that this provides a simple explanation for the observed luminescence of the anhydrides.

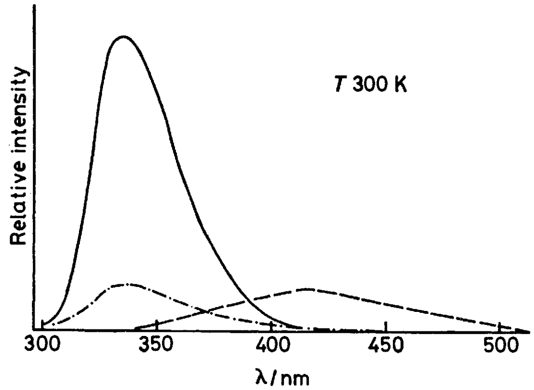


FIGURE 4 Emission spectra of 1-methylnaphthalene (———), 1,3-di-(1-naphthyl)propan-2-one (– – –) and 1-(1-naphthyl)-propan-2-one (— · — · — ·) in acetonitrile. Excitation wavelength 295 nm

The excimer emission is structureless as the transition is from the excited state to the quasi-continuum of the ground state.

1-(1-*Naphthyl*)*propan*-2-*one and* 1,3-*di*-(1-*naphthyl*)-*propan*-2-*one*. It is of interest to compare the luminescence behaviour of the naphthyl-substituted acetic anhydrides with that of naphthyl-substituted propanones. In Figure 4 the room-temperature emission spectrum of 1-methylnaphthalene (fluorescence) is shown together with those of a mono- as well as a 1,3-di-naphthyl-substituted propan-2-one.

Whereas the mononaphthyl-substituted propanone shows a greatly reduced fluorescence at *ca.* 340 nm typical of monomeric naphthalene, the 1,3-dinaphthyl-substituted propanone (2a) fluoresces weakly at 400—450 nm, the region typical of intramolecular naphthalene excimer fluorescence or the carbonyl type of fluorescence.* Thus in spite of the presence of a potentially strong fluorescent label in (2a) (in which the two naphthyl groups are separated by 4 σ bonds) as well as in 1-(1-naphthyl)propan-2-one, both the naphthalene monomer fluorescence and the intramolecular excimer fluorescence

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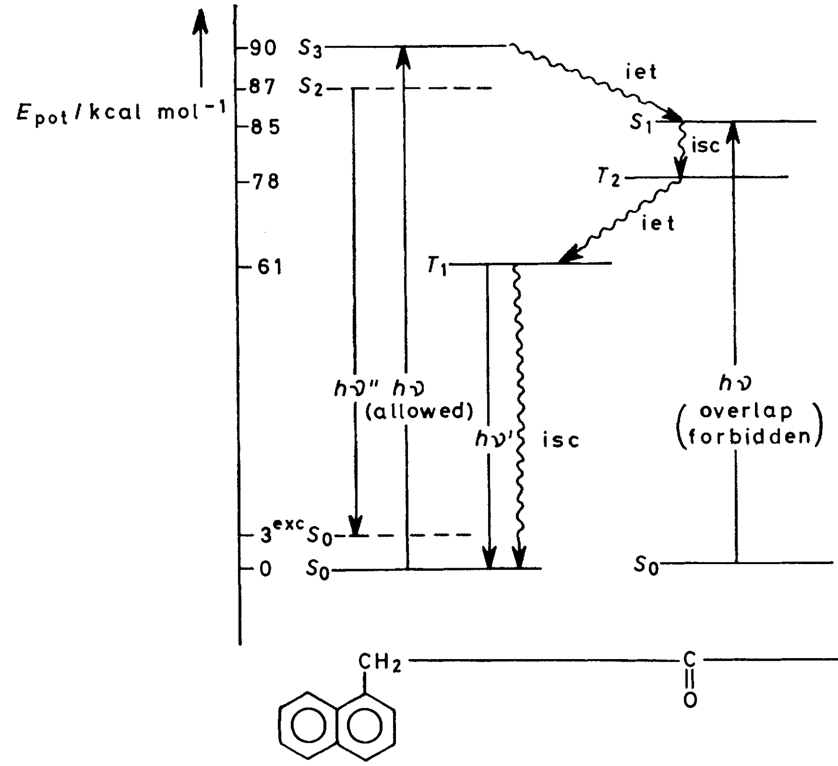
* It is highly unlikely that normal carbonyl fluorescence is observed at the concentration level used (10^{-5}M). Also the negligible fluorescence of 1-(1-naphthyl)propan-2-one in this region (see Figure 4) strongly disfavours such an assignment.



SCHEME 3 Hypothetical energy diagram for 1,3-di-(1-naphthyl)propan-2-one; i.e.t. stands for intramolecular energy transfer. Excimer states are indicated by dashed lines

are remarkably weak! Apparently there is another mode of deactivation for the singlet excited states of the naphthyl chromophore. As discussed before, it is very likely that deactivation occurs by internal conversion as a result of intramolecular energy transfer to the carbonyl group.

In Figures 5 and 6 the emission of low temperature glasses of 1-methylnaphthalene and 1,3-di-(1-naphthyl)-propan-2-one (2a) are depicted. The ketone exhibits essentially no naphthalene monomer fluorescence; the phosphorescence of the ketone appears, however, to be mainly of the naphthalene monomer type. The resemblance to spectra reported by Chandross for 1,3-di-(1-naphthyl)propane supports this assignment and suggests that little influence, if any, is exercised by the ketone function on the behaviour of the excited naphthyl chromphore.

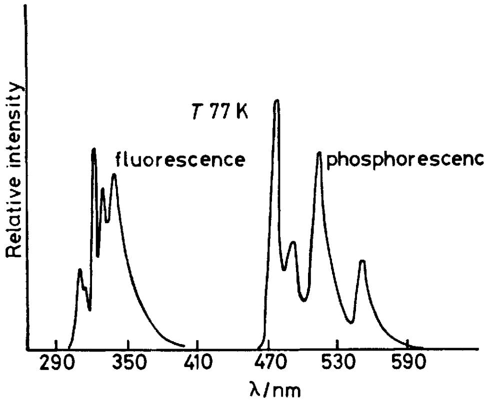


FIGURE 5 Emission spectrum of 1-methylnaphthalene at 77 K in isopentane–methylcyclohexane (4 : 1)

In Scheme 3 the behaviour of ketone (2a) is rationalised by an energy diagram, in which the naphthyl and carbonyl functions are considered to be essentially isolated (*cf.* refs. 3, 5, and 6). The lowest excited singlet state S_1 is probably mainly located on the carbonyl group. The singlet state of the intramolecular naphthalene excimer will be at least of about equal energy as that of the carbonyl singlet state, but is presumably of slightly higher energy content and is therefore referred to as the S_2 state. The excited state designated as S_3 which is comparable with the S_1 state of naphthalene proper may give rise to monomer fluorescence of the naphthyl group,

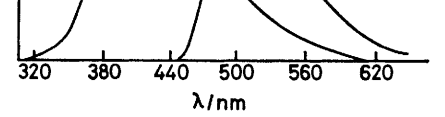


FIGURE 6 Emission spectrum of 1,3-di-(1-naphthyl)propan-2-one at 130 K in a 2-methyltetrahydrofuran glass

but is proposed to be quenched by intramolecular energy transfer (i.e.t.) to the S_1 state.

Emission from the S_2 state will compete with other modes of deactivation within the molecule. The relevant naphthalene excimer states ($^{\mathrm{exc.}}S_0$ and $^{\mathrm{exc.}}S_1 = S_2$) are indicated in Scheme 3 by dashed lines.

It is of interest that no excimer fluorescence was observed with 1,3-diphenylpropan-2-one,[17] a compound exhibiting a very efficient photodecarbonylation *via* the triplet excited carbonyl state.[3] It is further noteworthy that Wagner observed efficient intermolecular energy transfer from (monomeric) 1-methylnaphthalene to aliphatic ketones, despite extensive naphthalene excimer formation in the concentration range studied.[6] Wagner further observed a roughly equal degree of quenching of both monomer and excimer fluorescence of 1-methylnaphthalene by the carbonyl compounds, but considered that the energy transfer involved only the excited monomer.

Further inspection of the spectra presented in Figures 5 and 6 shows that ketone (2a) compared with 1-methylnaphthalene exhibits some additional phosphorescence at longer wavelengths (500—600 nm). This emission may originate either from the intramolecular excimer function or the carbonyl group of triplet excited (2a), or from both. Tentatively it is assigned to excimer emission, in view of the efficient quenching of the carbonyl triplet by naphthalene [6] and the formal argument that the naphthalene excimer is not quenched by naphthalene itself. A similar effect was reported by Subudhi and Lim [18] for the emission of 1,3-di-(1-naphthyl)propane. For naphthalene itself the intermolecular excimer phosphorescence is at *ca.* 550 nm.[19,20]

Without an extension of the investigation into the quantitative aspects of these photophysical processes, one can only speculate as to the origin of excimer phosphorescence of ketone (2a), *i.e.* whether it occurs from triplet excimer formed by intersystem crossing, or from triplet carbonyl.

EXPERIMENTAL

Materials.—Carboxylic anhydrides were prepared from the parent carboxylic acids by refluxing in acetic anhydride and removal, by distillation, of the resulting acetic acid.[21] 1-Naphthylacetic anhydride had m.p. 116° (lit.,[22] 116°); $\nu_{\max.}$ ($CHCl_3$) 1 810 and 1 745 cm^{-1}; δ ($CDCl_3$) 7.0—8.0 (14 H, m, ArH) and 4.04 (4 H, s, CH_2); $\lambda_{\max.}$ (CH_3CN) 281.5 nm (ε 14 000) (Found: C, 81.5; H, 5.0; O, 13.7. Calc. for $C_{24}H_{18}O_3$: C, 81.3; H, 5.1; O, 13.5%).

2-*Naphthylacetic anhydride* had m.p. 126—129°; $\nu_{\max.}$ ($CHCl_3$) 1 820 and 1 750 cm^{-1}; δ ($CDCl_3$) 7.1—7.85 (14 H, m, ArH) and 3.84 (4 H, s, CH_2); $\lambda_{\max.}$ (CH_3CN) 277 nm (ε 14 700); *m/e* 310 ($M^+ - CO_2$) and 168 (100%) (Found: C, 81.2; H, 5.0; O, 13.4. $C_{24}H_{18}O_3$ requires C, 81.3; H, 5.1; O, 13.5%).

1,3-Di-(1-naphthyl)propan-2-one was prepared in low yield according to the method of King and McMillan,[22] m.p. 109—110° (lit.,[22] 108—109°); $\nu_{\max.}$ ($CHCl_3$) 1 710, 1 600, 1 500, and 1 420 cm^{-1}; δ ($CDCl_3$) 7.08—8.08 (14 H, m, ArH) and 4.10 (4 H, s, CH_2); $\lambda_{\max.}$ (CH_3CN) 295 (ε 11 950), 283 (15 930), and 273 nm (12 800); *m/e* 310 (M^+), 282, 169, 141, and 115 (Found: C, 89.0; H, 5.8. Calc. for $C_{23}H_{18}O$: C, 89.0; H, 5.8%). 1-(1-*Naphthyl*)*propan*-2-*one* was prepared by reaction of 1-naphthylacetic acid with methyllithium in ether at 0°,[23] b.p. 120—130° at 0.01 mmHg (Kugelrohr distillation apparatus); $\nu_{\max.}$ (neat) 1 700 cm^{-1}; δ (CCl_4) 7.25—7.90 (7 H, m, ArH), 3.95 (2 H, s, CH_2), and 1.95 (3 H, s, CH_3).

All compounds and solvents employed in the luminescence experiments were purified carefully by repeated crystallization and distillation, respectively. Samples were degassed by four freeze–pump–thaw cycles on a vacuum line (10^{-5}—10^{-6} mmHg) before use in the low temperature experiments.

Luminescence Measurements.—Three experimental set-ups have been used. The first consisted of a Zeiss ZFM 4C spectrofluorometer. The excitation wavelength was selected from the emission of either a high-pressure xenon arc (Osram XBO 450 W) or a low pressure-mercury arc (Hanau ST 40, 150 W), by use of a Zeiss M4QIII monochromator. The sample was placed in front of the slit and the fluorescence was detected at right angles to the incident radiation beam by an EMI 9785 photomultiplier *via* a second motor-driven M4QIII monochromator. The signal was amplified by a Zeiss PMQII amplifier and recorded on a Philips PM 8100 multi-range recorder.

The second set-up was used for comparison of the fluorescence spectra of 1-methylnaphthalene, 1,3-di-(1-naphthyl)propan-2-one and 1-(1-naphthyl)propan-2-one, and consisted of a Shimadzu RF-500 spectrofluorometer with a Xenon lamp as radiation source. Emission and excitation bandwidths were both fixed at 10 nm.

The third set-up was employed for experiments with 1-methylnaphthalene and 1,3-di-(1-naphthyl)propan-2-one at 77 and 130 K, respectively. These temperatures were chosen in order to obtain a glass with the solvents used. The desired excitation radiation was selected from a 1 600-W xenon lamp (AEG type XBO) by a quartz double chromator (Zeiss MM 12). The emission was detected *via* an M 20 grating monochromator (Zeiss) for which a photomultiplier of the type S-20 (EMI 9558 QA) was used. The signal was amplified by a photon quantisizer (Par 231) and recorded on a Philips PM 8100 recorder.

The samples were cooled by either immersing the quartz cuvette directly in liquid nitrogen, or by gradually cooling the sample in a polyurethane-isolated stainless steel Dewar, equipped with vacuum-isolated quartz windows. In the latter case cooling was achieved by a stream of cold nitrogen gas delivered from a Cryoson CT-25-R self-pressurizing liquid nitrogen Dewar and regulated by means of a Cryoson TRL-3 temperature control unit or a Cryoson TRL-4 unit. Condensation of water vapour was prevented by electric heating of the outer windows.

Instruments.—I.r. spectra were recorded on a Perkin-Elmer 125 or a Unicam SP 200 spectrometer. ^{1}H N.m.r. spectra were recorded on a Varian A-60D, HA-100, or XL-100 spectrometer, using tetramethylsilane as internal standard. U.v. spectra were obtained with a Cary 14 or a Shimadzu UV-200 instrument and mass spectra were obtained with either a Varian MAT-711 or an AEI MS-902 mass spectrometer equipped with an all-glass heated inlet system. The electron energy was 70 eV. Irradiations were carried out in a Rayonet photochemical reactor (254 nm, RPR 100; 300 nm, RPR 208) equipped with 16 RPR 2537 and 8 RUL 3000 lamps respectively.

Product Analyses.—Products were identified by comparison of their spectral data and/or physical constants with those of authentic samples [as for (2a)], or with those described in the literature [as for (2b),[24] (3b),[4] (4a), [25-27] and (4b).[4,24,25]]. Compound (3a) was identified from the following spectral data, δ ($CDCl_3$) 7.20—8.10 (14 H, m, ArH), 5.17 (2 H, s, CH_2O), and 4.02 (2 H, s, CH_2CO).

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