Photocycloaddition of Cyanonaphthalenes with Acetylacetone: Enhancement of Quantum Yields by Sulphuric Acid

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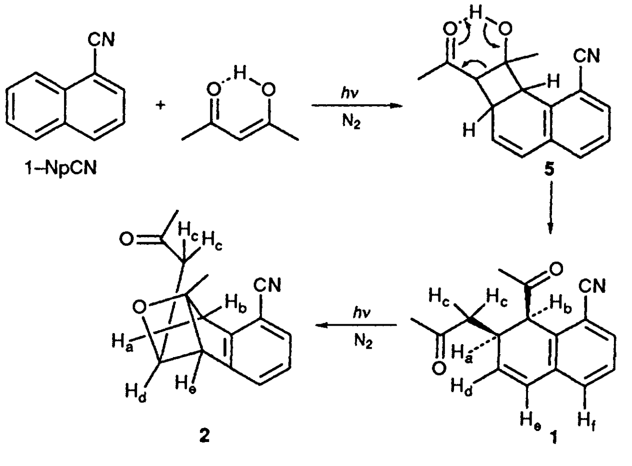
In acetonitrile or methanol, singlet excited 1-cyano- and 2-cyano-naphthalenes (1-NpCN and 2-NpCN) react with acetylacetone to give vicinally substituted acetyl–acetonyl addition products, **1** and **3**, that are assumed to be formed by a [2 + 2] photocycloaddition followed by ring opening. The diketone **1** was photolysed to give an oxetane by an intramolecular addition reaction. The photocycloaddition was quenched by typical singlet quenchers such as tributylamine, dimethylaniline, biacetyl, oxygen and methyl iodide; these substrates also quenched cyanonaphthalene fluorescence. The rate constant for the interaction of singlet excited 2-NpCN, determined by monitoring the quantum yield of **3**, was much smaller than that obtained by monitoring fluorescence intensities. Therefore, the reactive species is related to the spectroscopic singlet state but by an unknown mechanism. The quantum yields of the photocycloadditions of NpCN were remarkably enhanced in the presence of H_2SO_4 at $\leq 10^{-3}$ mol dm^{-3}. Over this sulphur acid concentration in acetonitrile, the fluorescence intensitity of *2-NpCN was not significantly affected; at higher sulphur acid concentration (0.0006–0.03 mol dm^{-3}), the quenching by H_2SO_4 was analysed by the Stern–Volmer relation to give a rate constant of 0.55×10^9 dm^3 mol^{-1} s^{-1}, a relatively low value.

We have discovered that during photoexcitation acetylacetone not only adds to naphthols and their methyl ethers,[1] but also to naphthoate esters[2] through a [2 + 2] photocycloaddition mode. The photocycloaddition is interesting owing to the fact that both reactants have been shown to be photoreactive.[3–8] It is also surprising since naphthalene derivatives of opposing electronic characters can undergo similar reactions,[9–13] although the site of reaction is different. The cyclobutane intermediates, generally assumed to be the primary photoadducts, are not stable enough to be isolated but rearrange to give vicinally substituted acetyl–acetonyl adducts. The pattern of this photocycloaddition is analogous to the de Mayo reactions known to occur between enols of 1,3-diketones and simple alkenes,[3,4,14,15] and is also a potentially useful reaction with synthetic applications. In this paper we wish to describe the reactions of 1- and 2-naphthonitrile (1-NpCN and 2-NpCN) with acetylacetone (acacH) and the factors controlling these reactions. The photophysics[16–18] and photochemistry of naphthonitriles[9–13] in the presence of simple electron-rich alkenes (such as tetramethylethylene) have been extensively studied as a model to demonstrate the intermediacy of exciplexes in the formation of cycloaddition products. Taking advantage of the strong fluorescence exhibited by naphthonitriles, the decay kinetics of the fluorescence intensities were extensively investigated to show the kinetics of excited states and their exiplexes.[10,16] For example, the lifetimes of singlet-excited 1-NpCN was shown to be 18.3 ns but that of the 1-NpCN-tetramethylethylene exciplex only 3.3 (or 3.75) ns.[16] As far as we are aware, photoreactions of naphthonitriles with an enone have not been reported.

Table 1 Excited state parameters of naphthonitriles[a]

	1-NpCN	2-NpCN
Absorption maxima (ε/nm)	321 (1970) 305 (5100) 294 (7050) 282 (5400)	329 (1250) 315 (930) 279 (5850) 272 (4500)
Fluorescence maxima/nm	332, 342	337, 350, 365 (sh)
Singlet state energy/kcal mol^{-1}	87 (329 nm)	86 (333 nm)
Lifetime of singlet excited state/ns[b]	11.0	24.4
Triplet state energy/kcal mol^{-1}	57 (504 nm)	58 (490 nm)

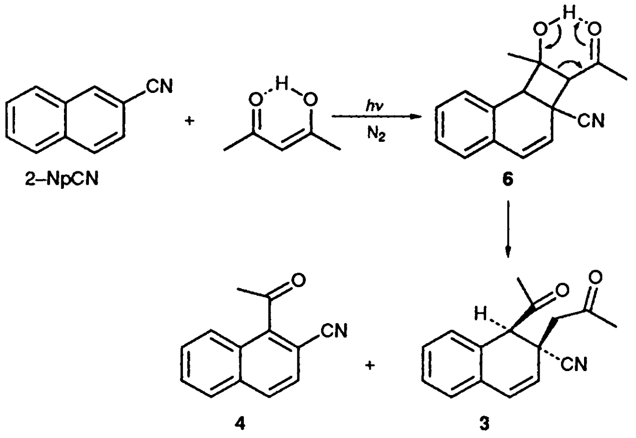
[a] The phosphorescence spectra were determined in isopropyl alcohol–ether (1 : 3) at 77 K and the absorption spectra in methanol; fluorescence and related data were measured in acetonitrile at 25 °C. [b] Determined by oxygen (1.1×10^{-3} mol dm^{-3}, air) quenching[19,20] using $k_q = 3.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1} in acetonitrile.[21]



Results

Absorption maxima of 1-NpCN and 2-NpCN are shown in Table 1. The photoreaction of the naphthonitriles was mostly carried out in acetonitrile or in methanol. Photolysis of an acetonitrile solution of 1-NpCN and acacH under nitrogen with Rayonet 300 nm lamps for 18 h caused slow disappearance of 1-NpCN (85%) and gave 1-cyano-7-acetonyl-8-acetyl-7,8-dihydronaphthalene (**1**) as the major product in addition to several trace-amount products (< 3%) as shown by GC analysis; this diketone **1** in acetonitrile was further photolysed with a Hanovia lamp through a Pyrex filter to give 2-acetonyl-6-cyano-7a-methyl-2,2a,7,7a-tetrahydroindeno[2,1-*b*]oxete (**2**). The structure of **1** was shown to have two isolated carbonyl groups by the presence of a strong IR absorption at 1715 cm^{-1} and ^{13}C NMR signals at 206.3 and 204.7 ppm. The ^{1}H NMR spectrum showed conjugated alkenic protons at 5.87 and 6.44 ppm (H_d and H_e, J = 10 Hz) and H_a at 3.43 ppm. By decoupling experiments, H_a was shown to couple to H_d and two magnetically very similar H_c protons (at 2.8 ppm) and also to H_b; the value of J_{ab} = 6 Hz indicated a *cis*-orientation of H_a and H_b. Irradiation of H_e caused large enhancement of H_f and H_d couplings. In contrast, compound **2** showed the presence of only one acetyl group, as evidenced by a ^{13}C NMR signal at 207.2 ppm and a methyl singlet at 2.18 ppm. Together with the absence of alkenic signals in the ^{1}H and ^{13}C NMR spectra, this indicates intramolecular oxetane formation, as shown. It was demonstrated by decoupling experiments that H_e (d, 4.67 ppm, J 3.5 Hz) was coupled to H_d (dd, 3.91 ppm, J 3.5 and 1.5 Hz), and that H_a (at 1.91 ppm) was coupled to two geminal diastereotopic H_c at 3.02 ppm (dd, J 9 and 18.5 Hz) and at 2.87 ppm (dd, J 5.5 and 18.5 Hz). As the chemical shifts showed that the geminal protons must be the CH_2 protons of the acetonyl group, this provided a confirmation of structure **2**. The lack of vicinal coupling for H_a–H_b may be ascribed to dihedral angle factors. The unusually deshielded benzylic H_e proton may arise from the near coplanarity with the benzene ring which exerts anisotropic effects.

Similar photolysis of a methanol solution of 2-NpCN and acacH under nitrogen for 16 h caused the disappearance of 50% of 2-NpCN and gave 1-acetyl-2-*cis*-acetonyl-2-*trans*-cyano-1,2-dihydronaphthalene (**3**) and one minor product in a 4:1 ratio. The minor product was assumed to be 1-acetyl-2-cyanonaphthalene (**4**) from the GC–MS data (M^+ 195). Other trace products showing tiny GC peaks were not studied. The structure of **3** must have two separate acetyl groups as evidenced by ^{1}H NMR methyl singlets at 2.12 and 2.22 ppm, ^{13}C NMR signals at 204.38 and 204.11 ppm and a strong IR absorption at 1728 cm^{-1}. An AB quartet at 3.06 and 3.46 ppm (J = 17.5 Hz) for the diastereotopic methylene protons and a singlet at 4.49 ppm for the benzyl proton clearly define the structure **3**; the alternative addition mode would generate a typical ABX coupling pattern for these protons. Compound **3** was analogous to a photocycloaddition product obtained by acacH and methyl 2-naphthoate and exhibited the same spectral features.[1] However, in the present case the *cis*-configuration of the acetyl and acetonyl groups was assumed from the proposed [2 + 2] cycloaddition mechanism without experimental evidence. Compound **4** was most likely derived from a secondary photoreaction, the Norrish Type II elimination of acetone from excited state **3**. Indeed, the yield of **4** increased as the percentage conversion increased.



These photocycloadditions occurred fairly slowly requiring a long irradiation time in order to give reasonable yields. The quantum yields of the photocycloadditions in acetonitrile were dramatically increased in the presence of trace amounts of sulphuric acid; *e.g.*, in the presence of H_2SO_4 at concentrations of 0.0, 0.0003 and 0.001 mol dm^{-3}, the relative yields of **1** measured in a merry-go-round were 1:6.7:8.5 and those of **3** were 1:2.1:2.8 determined under the same conditions. The quantum yield enhancement by H_2SO_4, however, rapidly attenuated above 0.001 mol dm^{-3}.

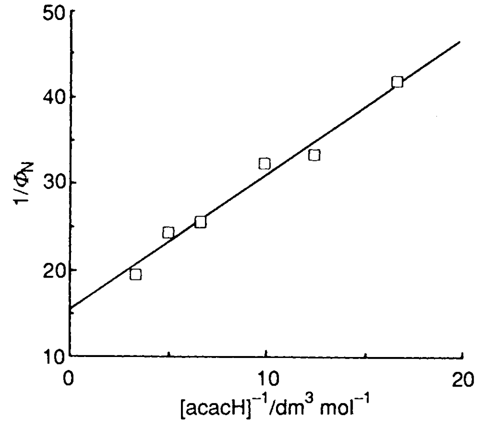


Fig. 1 The plot of Φ_N^{-1} *vs.*[acacH]$^{-1}$ where Φ_N is the quantum yield for 2-NpCN disappearance in the photoaddition with acetylacetone (acacH) in acetonitrile

The photocycloaddition of 2-NpCN with acacH was further investigated by quantum yield determinations in acetonitrile and its kinetic analysis in the presence of increasing amounts of acacH (0.06–0.30 mol dm^{-3}). The double reciprocal plot of Φ_N^{-1} *vs.* [acacH]$^{-1}$, according to eqn. (1) gave a limiting quantum yield

$$\Phi_N^{-1} = \Phi_{lim}^{-1}\left(1 + \frac{1}{K_{sv}[acacH]}\right) \qquad (1)$$

for the disappearance of 2-NpCN with Φ_{lim} = 0.065 ± 0.005 and K_{sv} = 10 ± 1 (Fig. 1); Φ_N in the present case is the quantum yield for 2-NpCN disappearance. The quantum yield for the formation of **3** was reduced efficiently in the presence of either air (oxygen) or low concentrations (<0.01 mol dm^{-3}) of dimethylaniline, tributylamine (TBA), biacetyl and methyl iodide. For a photocycloaddition system containing 2-NpCN (0.02 mol dm^{-3}) and acacH (0.08 mol dm^{-3}) in acetonitrile under nitrogen the quantum yields of **3** were determined both in the presence (Φ) and absence (Φ^0) of TBA, and analysed by the Stern–Volmer eqn. (2) to afford K'_{sv} = 55 ± 3 (Fig. 2). For

$$\Phi^0/\Phi = I^0/I = 1 + K'_{sv}[Q] \qquad (2)$$

comparison, the photocycloaddition of acacH with cyclohexene, a typical de Mayo reaction, was not quenched at all by TBA. The quenching of the formation of **3** by methyl iodide did not yield a linear correlation owing to the complication from the decomposition of methyl iodide (*vide infra*). The present photocycloadditions of naphthonitriles did not occur with xanthone (E_T 74.1 kcal mol^{-1}) or benzophenone (E_T 69.2 kcal mol^{-1}) sensitization in which sensitizers absorbed all incident light.*

Both naphthonitriles exhibit strong fluorescence which has been used to examine excited state reactions extensively.[10,16,17] The pertinent data derived from absorption and fluorescence spectra of the naphthonitriles under discussion are summarized in Table 1. The lifetimes in acetonitrile were determined by

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* 1 cal = 4.184 J.

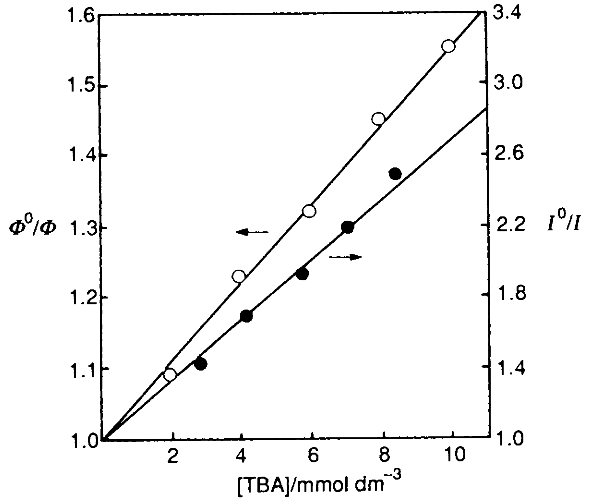

Fig. 2 The quenching of 2-NpCN fluorescence intensity (I^0) under air in acetonitrile and the quantum yield (Φ^P) of the photocycloaddition in acetonitrile of 2-NpCN (0.02 mol dm^{-3}) with acacH (0.08 mol dm^{-3}) by tributylamine (TBA)

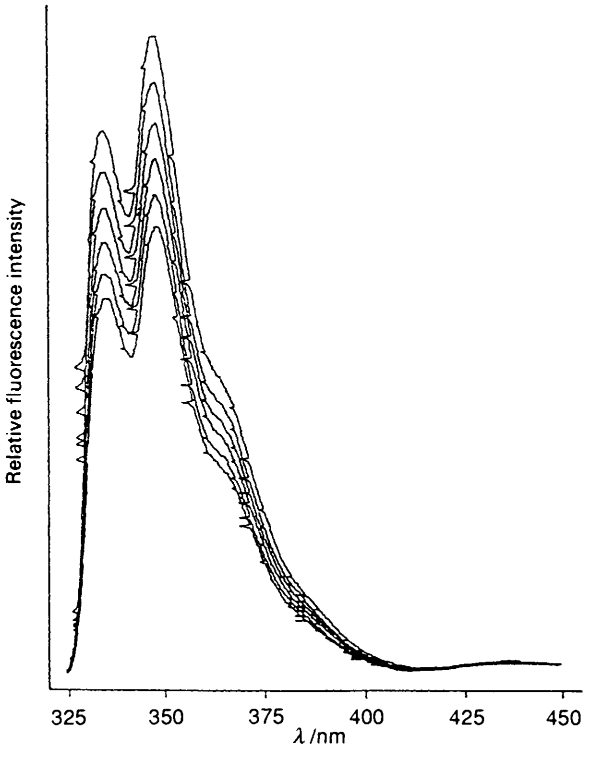

Fig. 3 The quenching of 2-NpCN (5.5 × 10^{-5} mol dm^{-3}) fluorescence intensity by H_2SO_4 (0, 0.0062, 0.0123, 0.185, 0.0247 and 0.0308 mol dm^{-3}) in acetonitrile under nitrogen; λ excitation at 320 nm

oxygen quenching.[19,20] The fluorescence intensity of 2-NpCN was reduced by acacH, TBA and methyl iodide in solution either purged or unpurged with nitrogen. Using the standard Stern–Volmer analysis of I^0/I *vs.* [Q] plots, as shown in eqn. (2), quenching constants K'_{sv} were determined. These K'_{sv} values were 57 ± 2 dm^3 mol^{-1} for acacH quenching under nitrogen, and 177 ± 5 (Fig. 2) and 44 ± 1 dm^3 mol^{-1} by TBA and methyl iodide, respectively, in the presence of air. From these data the interaction rate constant k_r of singlet excited state 2-NpCN with acacH could be calculated unambiguously since $K'_{sv} = 57 = k_r\tau^0$; using $\tau^0 = 24.4$ ns, this gives $k_r = 2.34 \times 10^9$ dm^3 mol^{-1} s^{-1}. The quenching rate constants by TBM and methyl iodide were also calculated by using a lifetime modified by oxygen interaction at the diffusion-controlled rate constant; k_q by TBA and methyl iodide quenching were calculated to be 1.42 × 10^{10} and 3.52 × 10^9 dm^3 mol^{-1} s^{-1}, respectively. However, in contrast to the promotion of the photocycloaddition, the fluorescence intensities of 2-NpCN were not visibly reduced in the presence of $[H_2SO_4] \le 0.001$ mol dm^{-3} in acetonitrile. Also, the absorption spectrum including the intensities of 2-NpCN in acetonitrile was not visibly changed in the presence of sulphuric acid at concentrations in the range 0.0006–0.031 mol dm^{-3}. Interestingly, in this concentration range (0.0006–0.031 mol dm^{-3}), the fluorescence intensities were reduced proportionally without showing a new peak (Fig. 3); the Stern–Volmer plot gave K_{sv} (= slope) = 13.4 ± 0.2 dm^3 mol^{-1}. The rate constant for the interaction of singlet-excited 2-NpCN (τ^0 = 24.4 ns) with H_2SO_4 was calculated to be 0.55 × 10^9 dm^3 mol^{-1} s^{-1}, a slow excited-state reaction. It should be added that eqns. (1) and (2) are derived on the bases of the assumption of excited-state reactions[20] involving unimolecular reactions modified by other bimolecular reactions.

Discussion

The formation of **1** from 1-NpCN and **3** from 2-NpCN indicates that the photoreaction occurs by [2 + 2] cycloadditions by an analogous pattern to the photoreaction of naphthoates and acacH reported previously.[1] The intermediates are the cyclobutanes **5** and **6** that spontaneously rearrange to give the ketones **1** and **3**. This intermediary would favour the *cis*-configuration in the final product for **1** and **3**, though no evidence has been obtained for the *cis*-configuration for **3**. While from structural points of view the product pattern resembles that of the de Mayo reaction,[14,15] mechanistically the present photocycloaddition is different in many respects. Firstly, the present reaction occurs from the singlet state of naphthonitriles, but not from an excited state of acacH (see below). Secondly, it occurs in polar solvents such as methanol and acetonitrile but not in cyclohexane and benzene; we have confirmed that the de Mayo reaction occurs in the latter type non-polar solvents,[3] but not in polar solvents of the former type. Thirdly, in contrast to the de Mayo reaction, it shows H_2SO_4 enhancement of the reaction product though the promotion mechanism is unclear at this stage.

A more quantitative treatment of the photocycloaddition mechanism has not been met with much success owing to difficulty in identifying the reactive excited state unambiguously. The double reciprocal plot of Φ_N^{-1} *vs* [acacH]$^{-1}$, with the calculation of Φ_N based on light absorbed by 2-NpCN, is compatible with the fact that the photocycloaddition is initiated by the excitation of 2-NpCN and the interaction of singlet-excited 2-NpCN with acacH. Reactions occurring from the triplet state of either substrates are not likely by failed triplet sensitization. In view of the short singlet excited lifetime of acacH, the most probable reactive species is singlet excited 2-NpCN. This is confirmed by TBA quenching of the photoreaction and 2-NpCN fluorescence (a quantitative treatment is discussed below) as opposed to the failure of TBA to quench the de Mayo reaction.

The photocycloaddition of 2-NpCN to acacH shows a K_{sv} value (10 ± 1 dm^3 mol^{-1}) which is far smaller than K'_{sv} (= 57 ± 2 dm^3 mol^{-1}) determined from the fluorescence quenching; this rules out single singlet-excited species of 2-NpCN covering the whole physical and chemical processes since such a case would predict the same K_{sv} value. In view of the well-established singlet state photoreaction (*vide infra*), the excitation and mutation of 2-NpCN in the singlet-excited manifold may be more complex than ordinary cases. Among other possibilities, it is believed that two independent singlet excited species of 2-NpCN, both showing very similar fluorescence patterns, are involved; it can be assumed that both species interact with acacH but only one pathway leads to **6** which shows $K_{sv} = 10 \pm 1$ dm^3 mol^{-1}. Such a system involves complex kinetic analysis depending on small changes in reaction patterns, and requires time-resolved fluorimetry to sort out two kinetic series. Further investigations by static methods on the interaction with acacH were not attempted, since the fluorescence intensity in such a system represents a sum arising from two species.

TBA generally interacts with excited state molecules with similar high rate constants by electron transfer.[22–24] We may assume the TBA quenching rates of singlet excited 2-NpCN to be the average of those of these two species. On the basis of this assumption, TBA quenching can be analysed quantitatively to confirm the singlet-state reaction of 2-NpCN. For TBA quenching of 2-NpCN fluorescence under air (Fig. 2), $K'_{sv} = k_q\tau' = 177 \pm 5$ where τ' is the lifetime τ^0 (24.4 ns) modified by oxygen interaction at the diffusion-controlled rate constant, *i.e.*, $\tau' = (1/\tau^0 + 3.5 \times 10^{10} \times 1.1 \times 10^{-3})^{-1} = 12.5$ ns. This gives the TBA quenching of 2-NpCN fluorescence a rate constant k_q of 1.42×10^{10} dm^3 mol^{-1} s^{-1}. The quenching of the formation of photocycloadduct **3** at [acacH] = 0.08 mol dm^{-3} by TBA gave $K'_{sv} = k_q\tau'' = 55 \pm 3$, where τ'' is the lifetime τ^0 modified by the reaction of acacH with excited state 2-NpCN ($k_r = 2.34 \times 10^9$ dm^3 mol^{-1} s^{-1}); *i.e.*, $\tau'' = (1/\tau^0 + 2.34 \times 10^9 \times 0.08)^{-1} = 4.37$ ns. The rate constant for the quenching of the formation **3** by TBA is, therefore, $k_q = 1.26 \times 10^{10}$ dm^3 mol^{-1} s^{-1} which agrees well with the value obtained above by fluorescence intensity measurements under such different conditions.

From a mechanistic point of view, TBA must quench singlet excited-state 2-NpCN by electron transfer,[22–24] and the agreement between two k_q measurements clearly indicates that photocycloaddition is a reaction derived from singlet-excited 2-NpCN. This conclusion is further supported by other quenching experiments. Methyl iodide interacts with singlet excited-state 2-NpCN by spin-orbit couplings of the heavy atom to enhance the singlet–triplet transition.[25] Naturally this interaction quenches the singlet-state reaction and has been substantiated by fluorescence intensity reduction (with $K'_{sv} = 44 \pm 1$ dm^3 mol^{-1}). The concurrent suppression of photocycloaddition product **3** clearly indicates that the formation of **3** arises from the singlet excited state of 2-NpCN as has already been concluded. It is known that the presence of methyl iodide in photolysis generates hydroiodic acid; in the present case this acid also catalyses the formation of **3**. Owing to this counter effect, the quenching of the quantum yield of **3** in the presence of methyl iodide does not afford a quantitative correlation. Finally, while the enhancement of the photocycloaddition by a trace amount of H_2SO_4 makes this photocycloaddition attractive for synthetic application, the lack of significant effects on 2-NpCN fluorescence intensities at sulphuric acid concentrations $\leq 10^{-3}$ mol dm^{-3} poses difficulties in interpretation and the design of experiments. This may indicate that H_2SO_4 interacts with a subsequent species derived from a spectroscopic singlet state; for example, if an exciplex of *2-NpCN-acacH is irreversibly formed and interacts with H_2SO_4, the effects cannot be seen by 2-NpCN fluorescence. It must be mentioned that the rate constant for the interaction of singlet-excited 2-NpCN with H_2SO_4 is relatively slow (0.55×10^9 dm^3 mol^{-1} s^{-1}) as shown by the fluorescence quenching. Until such a time as the reactive singlet excited-state of 2-NpCN is clear, an undertaking to investigate H_2SO_4 effects appears to be difficult.

The participation of an acid in excited-state reactions has been occasionally reported; for example, in the hydration of alkenes,[26] in photocycloaddition,[27] in enone photoreactions and in the fluorescence of aromatic compounds. Such acid promotion (or demotion) may prove to be an important factor in photochemistry.

Experimental

General.—Spectroscopic and GC analytical apparatus, as well as their operating conditions, were the same as those published in a similar study.[1b] Commercial products of 1-NpCN (Aldrich) and 2-NpCN (Kodak) were recrystallized from light petroleum (b.p. 35–60 °C) to give m.p. 36–38 and 61–63 °C, respectively; these samples were sublimed. Acetylacetone (BDH) was distilled. Coupling constants *J* are given in Hz throughout.

Quantum Yield Determination.—Quantum yields were determined with a Rayonet Photochemical Reactor equipped with 300 nm (or 350 mm) lamps (16 × 24 W), a fan and turntable. The light intensity absorbed by the naphthonitriles was calculated according to the molar absorbance at 300 nm using an equation derived previously.[1b] Benzophenone–benzhydrol actinometry and its determination were as described before.[1b]

1-*Cyanonaphthalene.*—A solution of 1-NpCN (300 mg, 1.96 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 cm^3) purged with nitrogen was irradiated in a Rayonet Photochemical Reactor, using 300 nm lamps, for 18 h. GC analysis (200–230 °C at 10 °C min^{-1}) of the photolysate showed 85% of 1-NpCN was consumed and one major peak and several small peaks; the latter were not studied. The residue was twice chromatographed on a silicic acid column using 42% and 30% ethyl acetate in hexane as eluent to give white crystals (66.9 mg, 14%) of cis-1-*cyano*-7-*acetonyl*-8-*acetyl*-7,8-*dihydronaphthalene* (**1**), which was recrystallized from ether: m.p. 94.5–96 °C; δ_H(CDCl$_3$) 2.03 (s, 3 H), 2.21 (s, 3 H), 2.83 (m, 2 H), 3.34 (m, 1 H), 4.06 (d, *J* 6.5, 1 H), 5.87 (dd, *J* 10 and 2, 1 H), 6.44 (dd, *J* 10 and 3, 1 H), 7.33 (m, 2 H) and 7.49 (d, 1 H); δ_C(CDCl$_3$) 206.3, 204.7, 136.9, 135.3, 134.8, 131.2, 130.7, 128.7, 125.7, 117.5, 112.6, 52.9, 44.6, 32.3, 30.2 and 29.5; ν_{max}(Nujol)/cm^{-1} 2230w, 1715s, 1360m, 1160m, 910m and 820m; MS (EI), *m/z* (%), 253 (*M*, 1), 210 (35), 196 (50), 168 (51), 153 (100) and 43 (75) (Found: C, 75.95; H, 6.10. Calc. for $C_{16}H_{15}O_2N$; C, 75.9; H, 6.0).

A solution of compound **1** (203 mg, 0.8 mmol) in acetonitrile (100 cm^3) was irradiated in a Hanovia photoapparatus (200 W medium-pressure lamp) under nitrogen for 19 h. The GC analysis (200–230 °C at 10 °C min^{-1}) of the photolysate showed two GC peaks at t_R 4.34 min (16%) for **1** and a new one at t_R 3.77 min (41%). The residue was flash chromatographed using 40% ethyl acetate in hexane as eluent to afford 2-acetonyl-6-cyano-7a-methyl-2,2a,7,7a-tetrahydroindeno[2,1-*b*]oxete (**2**) as a yellow oil (40 mg); δ_H(CDCl$_3$) 1.35 (s, 3 H), 1.91 (dd, 1 H, J 5.5 and 9), 2.18 (s, 3 H), 2.87 (dd, 1 H, *J* 18.5 and 5.5), 3.03 (s, 1 H), 3.02 (dd, 1 H, *J* 18.5 and 9), 3.91 (dd, 1 H, *J* 3.5 and 1.5), 4.67 (d, 1 H, *J* 3.5), 7.20 (dd, 1 H, *J* 7.5 and 8), 7.34 (d, 1 H, *J* 8 and 7.40 (dd, 1 H, *J* 7.5 and 1.5); δ_C 207.2, 156.1, 138.4, 129.8, 128.0, 126.9, 117.3, 107.4, 106.0, 79.8, 61.7, 54.8, 47.6, 42.6, 30.0 and 15.4; ν_{max}/cm^{-1} 2980m, 2940m, 2243m, 1718s, 1590w, 1440m, 1165m, 920m, 860m, 880m and 740m; MS (EI), *m/z* (%) 210 (10), 196 (5), 167 (15), 153 (28), 43 (100); (CI), 254 (*M* + 1, 100) and 236 (19).

2-*Cyanonaphthalene.*—A solution of 2-NpCN (300 mg, 1.96 mmol) and acacH (300 mg, 3 mmol) in methanol (50 cm^3) was purged with nitrogen and irradiated in a Rayonet Reactor equipped with 300 nm lamps for 16 h. GC analysis (150–230 °C at 10 °C min^{-1}) of the photolysate showed one major peak at t_R 7.93 min (29%) and one minor peak at 5.88 min [8%, GC-MS: 195 (M^+, 50%), 180 (100), 152 (50), 125 (17) and 75 (10) plus several minor peaks (<3%) at *ca.* 6–8 min which were not studied. The residue was flash chromatographed (30% ethyl acetate in hexane) and recrystallized from ether to give white crystals (50 mg) of 1-*acetyl*-2-cis-*acetonyl*-2-trans-*cyano*-1,2-*dihydronaphthalene* (**3**); m.p. 68–70 °C; δ_H(CDCl$_3$) 2.12 (s, 3 H), 2.22 (s, 3 H), 3.06 (d, J = 17.5, 1 H), 3.46 (d, J = 17.5, 1 H), 4.49 (s, 1 H), 5.38 (d, J = 10, 1 H), 6.58 (d, J 10, 1 H), 7.18 (m, 1 H) and 7.31 (m, 3 H); $\delta_C(CDCl_3)$ 204.38, 204.11, 131.90, 129.75, 129.68, 129.15, 129.08, 129.01, 127.76, 126.49, 120.61, 56,07, 46.71, 35.85, 30.36 and 29.49; ν_{max}(Nujol)/cm^{-1} 2245m, 1728s, 1177m and 1168m; MS (EI), m/z (%), 253 (M^+, 2), 210 (2), 196 (7), 180 (5), 153 (100), 141 (40) and 43 (50) (Found: C, 75.8; H, 6.04. Calc. for $C_{16}H_{15}O_2N$: C, 75.9; H, 6.0%).

Acknowledgements

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