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On the photochemical behaviour of some diarylpyrazolines

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Abstract

The excited state behaviour of 1-phenyl-3(2,4,6-trimethylphenyl)-4,5-dihydropyrazole (**1**) and of the corresponding 1-(4-diethylaminophenyl) (**2**) and 1-(4-morpholinophenyl) (**3**) derivatives has been explored. All of these compounds fluoresce efficiently and the Stokes shift (11.6×10^{-3} cm^{-1} with **1**) increases by $(2–3)\times10^{3}$ cm^{-1} with the introduction of the electron-donating groups. They are unaffected both by direct irradiation in deoxygenated solution or by photosensitization with benzophenone. Compounds **1** and **2**, but not **3** are dehydrogenated to the corresponding pyrazoles by irradiation in deoxygenated acetone. In air-equilibrated toluene, acetonitrile or ethanol, direct irradiation ($\lambda > 300$ nm) of these pyrazolines causes only a slow reaction. However, **2** and **3** are dehydrogenated by irradiation at 254 nm in toluene. **1** is dehydrogenated by singlet oxygen in a dye-sensitized reaction, but this is not the case with **2** and **3**, and these compounds act as physical quencher of singlet oxygen with no measurable reaction. The key factor for rationalizing these reaction is the low oxidation potential of the substrates. © 1997 Elsevier Science S.A.

Keywords: Pyrazolines; Scintillators; Photo-oxidation; Photo dehydrogenation; Singlet oxygen

1. Introduction

Δ^1-Pyrazolines (1*H*-4,5-dihydropyrazoles) have long been known for their strong fluorescence and count among the most largely used optical whiteners [1]. Substituents at positions 1 and 3 have a major effect on the luminescing properties, and most of the substrates studied are 1,3-diaryl-1*H*-4,5-dihydropyrazoles, for which fluorescence quantum yields are commonly >0.8 [2–6]. It has been demonstrated that steric hinderance to planarity in the ground state (e.g. introducing *ortho* substituents in 1,3-diphenyl derivatives) causes a blue shift in the absorption spectrum and virtually no effect on the fluorescence spectrum, and thus leads to a large Stokes shift (of the order of 10^4 cm^{-1}) [2,7]. This property makes such substrates convenient for monocomponent scintillating solutions, since the Stokes shift is large enough to make unnecessary the use of a second component for minimizing the superimposition between absorption and fluorescence spectra. Indeed, 1-phenyl-3-(2,4,6-trimethylphenyl)-4,5-dihydropyrazole (PMP) has come into use as a scintillator for ^{14}C and ^{3}H counting, and its convenience with respect to traditional scintillators has been demonstrated as well as its applicability as a polymer (e.g. polyvinyltoluene, polystyrene) dispersion in optical fibres [8]. Obviously, photostability is of the utmost importance for this use. Therefore, we presently report our recent work about the photoreactions of PMP and some of its derivatives.

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2. Results

The substrates studied were the 1-phenyl derivative **1** ≡ PMP and the corresponding 1-(4-diethylaminophenyl) and 1-(4-morpholinophenyl) derivatives (**2** and **3**). The last two derivatives were prepared in order to test whether substitution would further widen the Stokes shift observed with **1**. Absorption and corrected fluorescence spectra of compounds **1** to **3** are reported in Table 1 and Fig. 1. On the other hand, no phosphorescence was detected, nor was any tran-

Table 1
Absorption and fluorescence maxima about the pyrazoles and pyrazolines considered (in MeCN, 10^{-3} cm^{-1})

Compound	ν_a	ν_f	$\Delta\nu_{St}$
1	34.5	22.9	11.6
2	33.9	19.2	14.7
3	33.3	19.5	13.8
4	34.5	22.8	
5	35.1	25.6	

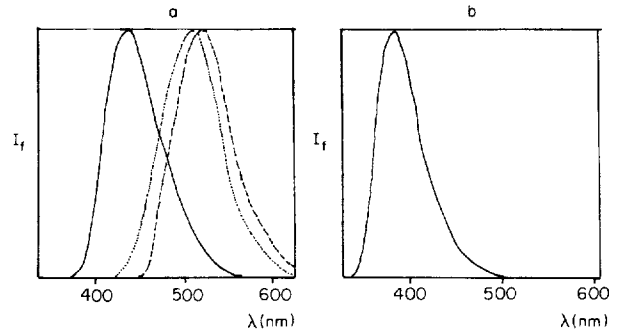


Fig. 1. (a) Corrected and normalized fluorescence (arbitrary units) spectra of the pyrazolines **1** (———), **2** (- - -), **3** (···). (b) Corrected fluorescence spectrum of the pyrazole **4**.

Table 2
Yield of chemical products

Substrate	Conditions	Products (% yield)
1	Me_2CO, $h\nu > 300$ nm, 10 h	**4** (70)
1	RB, MeCN, $h\nu > 300$ nm, 1 h	**4** (86)
2	Me_2CO, $h\nu > 300$ nm, 25 h	**5** (82), **6** (12)
2	$PhCH_3$, $h\nu$ 254 nm, 30 h	**5** (40)
3	$PhCH_3$, $h\nu$ 254 nm, 20 h	**7** (31)

sient observed by laser flash photolysis. Irradiation of these compounds in deaerated acetonitrile, ethanol or toluene solution at $\lambda > 300$ nm led to no measurable decomposition after several hours. With air-equilibrated solution a slow reaction took place, yielding a complex product distribution.

Irradiation of argon-flushed acetone solutions led to an efficient reaction with compounds **1**. A single photoproduct was isolated, and was shown to be the pyrazole **4** by its analytic and spectroscopic properties (see Section 4, Table 2 and Scheme 1). The reaction of compound **2** was slower, but rather clean, and gave the diethylaminophenylpyrazole **5** as the main product, accompanied by a minor amount of the corresponding monoethylamino derivative **6**. In a separate experiment, it was shown that irradiation in acetone of preformed **5** led to **6**. On the other hand, the pyrazoline **3** showed very little decomposition under this condition, with formation of a trace of the pyrazole **7** (see below) and of unidentified products.

Irradiation of air-equilibrated toluene solutions at 254 nm gave modest decomposition with **1**, while a rather efficient reaction took place with **2**, to give again **5** as the main product, as well as, although more slowly, with **3**, to give **7**.

Irradiation in acetonitrile in the presence of benzophenone (> 300 nm) caused very little decomposition of all of the above substrates. The reaction was carried out preparatively (in MeCN) with **1**, where the only product detected was benzopinacol (not measurably formed by irradiation of Ph_2CO for the same time in the absence of **1**).

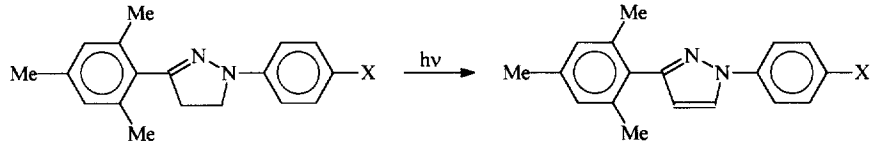
Visible light irradiation of an oxygen-equilibrated solution of **1** in MeCN in the presence of Rose Bengal led to a clean conversion to the pyrazole **4**. On the other hand, both **2** and **3** underwent only a very slow reaction, giving a trace of products **5** and **7**, respectively, under this condition. Further experiments included the measurement of the total quenching constant of singlet oxygen, directly measured via luminescence quenching, and, in the case of product **1**, the measurement of the rate of chemical reaction with singlet oxygen in acetonitrile by comparison with ottaline (for which the value determined in benzene was used). The results are reported in Table 3.

Some experiments were then carried out in order to test whether the pyrazoline–pyrazole conversion observed under some conditions could be obtained also thermally, in particular by radical initiators. It was found that, while AIBN is ineffective, *N*-bromosuccinimide converts **3** into **7** efficiently in refluxing acetonitrile.

Finally, voltammetric measurements showed a irreversible oxidation wave for pyrazoline **1** and a reversible wave for the two dimethylaminophenyl derivatives **2** and **3** (see Fig. 2). The evaluated oxidation potentials are listed in Table 3.

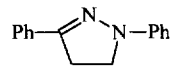
3. Discussion

The photophysics of arylpyrazolines has been extensively investigated, as one may expect in view of the great significance of these products as optical brighteners and scintillators. The relevant information for this study can be summarized as follows. These molecules fluoresce strongly (e.g. 1,3-diphenylpyrazoline, **8**, $\Phi_F = 0.75$, $\tau_F = 3.25$ ns in



1 X=H
2 X=NEt_2
3 X=Morpholino

4 X=H
5 X=NEt_2
6 X=NHEt
7 X=Morpholino



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Scheme 1.

Table 3
Redox parameters for the pyrazolines **1–3**

Substrate	E_{ox} (V vs. SCE)	ΔG_{et} (eV) [a]			k_q ($\times {}^1O_2$)	k_r ($\times {}^1O_2$)
		Me_2CO^{3*}	Ph_2CO^{3*}	$^1O_2$	($M^{-1}s^{-1}$)	($M^{-1}s^{-1}$)
1	0.91	+0.42	−0.26	+0.53	8.4×10^7	1×10^{6}[b]
2	0.26	−0.22	−0.92	−0.12		
3	0.35	−0.13	−0.83	−0.03	1.1×10^9	

[a] The ΔG_{et} for electron transfer was calculated according to the Weller equation, $\Delta G_{et}=E_{ox}(D)-E_{red}(A)-E_{exc}+e^2/\varepsilon\alpha$. For the oxidation potential of the pyrazolines, see above. For the reduction potential and excitation energies of the ketones and oxygen see Refs. [9–11]. In the case of acetone, the reduction potential in MeCN is assumed to be at −2.90 V vs. SCE, with respect to the reported value of −2.34 V in water, viz that the shift is similar to that observed for benzophenone in the two solvents.

[b] Based on competition experiments with ottaline. The rate constant measured for ottaline in benzene has been used, $1.84\times10^6\ M^{-1}s^{-1}$ [12].

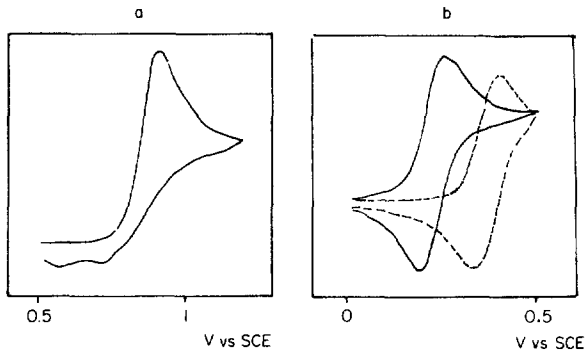


Fig. 2. (a) Cyclic voltammetry for pyrazoline **1**. (b) Cyclic voltammetry for pyrazolines **2** (———) and **3** (- - -). In every case the scan speed was 50 mV s^{-1}.

benzene) [2]. Substituting a mesityl for a phenyl ring in position 3 hinders planarity in the ground state and leads to a marked blue shift of the absorption spectrum and thus to a larger Stokes shift ($10.37\times10^3\ cm^{-1}$ for compound **1** vs. $4.98\times10^3\ cm^{-1}$ for parent **8**), but has otherwise little effect on the excited singlet state characteristics ($\Phi_F=0.70$, $\tau_F=3.01$ ns in benzene for **1**). As far as the triplet state is concerned, no monomolecular phosphorescence has been detected in glassy solvent at 77 K, but only a weak emission originating from associated species. On the basis of an indirect evidence, it has been proposed that the triplet of **8** is at 47–49 kcal mol^{-1} [13].

As for the photochemistry, Schrader reported that compound **8**, as well as 1,3,4- and 1,3,5-triphenylpyrazoline are photodehydrogenated to the corresponding pyrazoles by irradiation in air-purged benzene [14]. Evans observed the formation of pyrazoles from various pyrazolines both on direct irradiation and on dye-sensitization, and proposed a singlet oxygen mechanism [15–18]. Davidson raised doubts about the implication of singlet oxygen in the direct irradiation of **8** (for which he detected no triplet–triplet absorption), and found that observation of a solvent isotope effect is not necessarily an indication of such a mechanism [19].

3.1. Photophysics

As for the presently considered derivatives, the aminophenyl pyrazolines **2** and **3** show a minimal shift in the absorbance maximum and a marked red shift in the fluorescence maximum with respect to compound **1** (see Table 1). This effect is in the same direction as, although much larger than, that previously observed with other *p*-substituted 1-phenylpyrazolines (e.g. 1-(4-methoxyphenyl)-3-phenylpyrazoline shows $\nu_a(max)=27.03\times10^3\ cm^{-1}$, $\nu_f(max)=21.10\times10^3\ cm^{-1}$) [2]. This is rationalized with reference to the polarization from N_1 to N_2 existing in these compounds. The large Stokes shift observed with these amino derivatives ($(14–15)\times10^3\ cm^{-1}$) is thus understandable in view of the internal charge transfer character of the excited singlet of these compounds, and makes them suitable candidates for the use as scintillators.

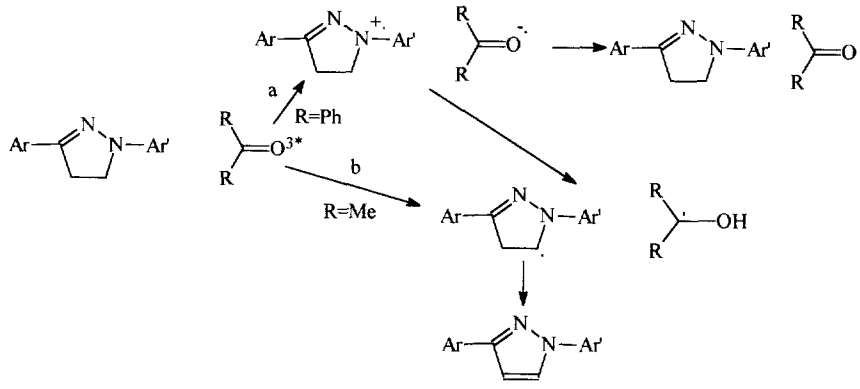
3.2. Photochemistry

The photochemistry has been explored in representative apolar, polar and protic solvent. Direct irradiation of these compounds is inefficient in all cases, and leads to some reaction only in oxygen-saturated solutions (see below). The lack of reactivity is understandable since emissive decay from the singlet accounts for the largest part of the absorbed quanta. It is doubtful whether a significant intersystem crossing takes place, since the present compounds, similarly to the pyrazolines previously tested [19], show neither phosphorescence nor triplet–triplet absorption in flash photolysis. At any rate, triplet states, if formed, have no radical character as shown by the lack of reactivity in deoxygenated alcohols.

On the other hand, these substrates under various conditions all undergo photodehydrogenation to the corresponding pyrazoles, which obviously limits their application as scintillators and leads to a new, blue-shifted fluorescence (see Fig. 1(b) for compound **7**). Although the chemical reaction remains the same along the series, the contrasting structure and conditions dependence observed with the three substrates studied suggest that different mechanisms are possible. The determining factor is in any case the easy oxidation of these compounds (see Table 3).

3.3. Photoreaction in the presence of ketones

Beginning with the reaction in the presence of ketones, the lack of reaction in the presence of benzophenone (under



Scheme 2.

conditions where only the ketone absorbs the light) can be rationalized with reference to Table 3. This shows that single electron transfer to benzophenone triplet is exothermic [9]. Thus, a radical ion pair is formed (Scheme 2, path a). However, no irreversible chemical reaction results, showing that pyrazoline radical cations do not undergo efficient deprotonation. Indeed, it has been shown that related radical cations (those of anilines) are relatively weak acids (for the dimethylamine radical cation the pK_a in MeCN is 9, and the value is higher with electron donating substituted dimethylanilines, which can be compared with compounds **2** and **3**) [20]. Thus, proton transfer is slow in the absence of a nucleophile [21,22]. The radical anion of benzophenone is formed, as indicated by the obtaining under this conditions of a little amount of pinacol arising from protonation of the radical anion by moisture present in the solvent. However, this species is not sufficient basic [22,10] to make proton transfer from the pyrazoline radical cation fast enough to overcome back electron transfer (see also below). As a result, physical decay to give the ground state reagents is the main path for the radical ion pair (Scheme 2).

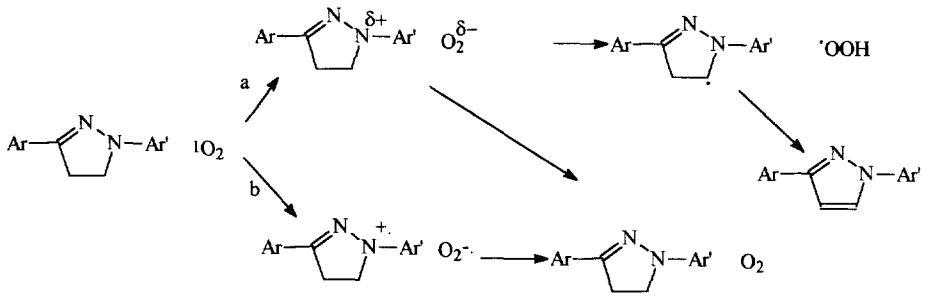
On the other hand, pyrazolines **1** and **2** react upon irradiation in acetone (again, the ketone absorbs the light). The interpretation here is less straightforward, since the reduction potential of acetone in MeCN has not been reported, and the value in water [10] is expected to be much less negative than that in MeCN. An estimate shown in Table 3 suggests that electron transfer exothermic also in this case with **2** and **3**, while it is endothermic with **1**. Thus, with **1** the reaction may be initiated by hydrogen abstraction (Scheme 2, path b), but with **2** single electron transfer is still the first step (path a). That compound **2** react in this case and not with benzophenone can be attributed to the stronger basicity of the acetone radical anion with respect to the delocalized radical anion of benzophenone, which makes proton transfer competitive with back electron transfer. Indeed, the reported pKa for the conjugate acids in water are 12.2 for the $Me_2COH^{\cdot}$ radical and 9.2 for the $Ph_2COH\cdot$ radical [10]. In an aprotic solvent, both radical anions are expected to be stronger bases, but the difference remains.

It is noteworthy that in the case of compound **2** proton transfer from the ring-methylene largely overcomes that from the diethylamino group, giving **5** as the only detectable primary photoproduct. Only after the first dehydrogenation step leading to aromatization of the pyrazoline ring does hydrogen transfer from the diethylamino group takes place, yielding **6** as a secondary photoproduct from **5** (see separate irradiation).

This suggests that the conformation of the initial caged radical ion pair determines the chemoselectivity, since back electron transfer cuts down any process not sufficiently fast. The fact that pyrazoline **3** is not rearomatized in acetone may be explained by a conformation unfavourable to proton transfer from position 4 (the morpholino group is less bulky than the diethylamino group, and this may alter the preferred conformation, with the acetone anion now closer to the exo amino function). That **3** is slowly consumed under this condition probably depends on the occurrence of different reactions involving the morpholino moiety.

3.4. Dye-sensitized reaction

The dye-sensitized reaction involves singlet oxygen. The chemical reaction of **1** is pyrazoline ring rearomatization, just as previously reported with parent **8** [14,15,19]. The reaction is slow and the chemical yield of **4** is unsatisfactory owing to its further decomposition at a long irradiation time. The total rate for quenching of singlet oxygen ($8.4\times10^7\ M^{-1}\ s^{-1}$) is much higher than that for chemical reaction, with physical quenching approaching 99%. This may be compared with similar easily oxidized substrates, e.g. dialkylanilines which have a similar total quenching rate for singlet oxygen (e.g. for *N,N*-dimethylaniline a value of $7.3\times10^7\ M^{-1}\ s^{-1}$ has been reported), and for which physical quenching appears to be the only mechanism [23]. With **1**, this predominates again, but some chemical reaction takes place. This can be rationalized as proton transfer from the pyrazoline to singlet oxygen within a strongly polarized complex (Scheme 3, path a). The primary chemical process is clean, although at increasing conversion secondary reactions of **4** complicate the product distribution. Apparently, the thermodynamic drive towards the fully conjugated system precludes the path to the other products one may have anticipated, such as 3-pyrazolones or



Scheme 3.

ring-cleaved derivatives, which are not formed in detectable amounts.

On the other hand, dye-sensitization is ineffective with the pyrazolines **2** and **3**. The total quenching rate grows by over one order of magnitude, but chemical reaction does not occur to a measurable extent. As one can see from Table 3, in this case electron transfer is exothermic, thus a radical ion pair rather than a polarized complex is formed (Scheme 3, path b). The superoxide anion is a moderate base in water (pK_a of the conjugate acid is 4.8), and although it has been estimated that it is stronger in apolar solvents ($pK_a = 12$) [11] this is not sufficient for fast proton transfer, and thus, just as in the benzophenone case, the radical ion pair undergoes no chemical reaction, although the initial quenching of singlet oxygen is fast (see Table 3). These pyrazolines act as purely physical quenchers of singlet oxygen. Thus, a charge transfer interaction allows some chemical reaction (proton transfer within the complex), but full electron transfer precludes it.

3.5. Photoreaction in oxygenated solutions

The decomposition of **1** by direct irradiation in oxygenated solutions may occur, as suggested for parent **8** [15], via a self-sensitized singlet oxygen path. However, this is certainly not the case for the slow dehydrogenation occurring with compounds **2** and **3** in aerated toluene solutions, since, as has been shown above, the singlet oxygen reaction is too slow in this case. It is noteworthy that the reaction occurs only by short-wavelength irradiation, viz when the solvent absorbs the light. Thus, the reaction is due to the generation of hydroxy or peroxy radicals under this conditions, reasonably via irradiation of the toluene–O_2 complex [24,25].

$$PhMe\cdots O_2 + h\nu \rightarrow PhCH_2^{\bullet},\ PhCH_2O_2^{\bullet},\ OOH^{\bullet}$$

$$\rightarrow \text{radical initiated reactions}$$

In accordance with this rationalization, when a ground state radical initiator is used, aromatization of the pyrazole ring is obtained also in the case of compound **3**, which thus does not differ from parent **1** as far as the liability to radical attack is concerned, even though it is more stable to photosensitized conditions (both ketone triplet and singlet oxygen). This lability is important from the applicative point of view, since such molecules are candidates for being used as scintillators as dopant in polystyrene [26], of which the toluene solution is a model.

3.6. Conclusion

In conclusion, introducing a 4′-dialkyamino substituent in 1-phenyl-3-mesitylpyrazolines causes a marked red-shift of the fluorescence, thereby increasing the Stokes shift via an electronic effect. This substitution makes the molecules very good donors, and this increases their photostability, since the observed efficient quenching of both singlet oxygen and excited ketones involves electron transfer and leads to physical decay rather than to chemical reaction. These molecules are still liable to radical attack, and this remains a path to rearomatization; however, such a pathway is operative only under particular conditions, e.g. short-wavelength irradiation of a toluene solution.

4. Experimental

The pyrazolines **1–3** were prepared and purified as separately reported [26].

The photochemical reaction were carried out in an immersion well apparatus (200 ml) by irradiation by a Pyrex-filtered medium pressure mercury arc (125 W) while flushing with argon or oxygen. Rose Bengal (10 mg/200 ml) sensitized experiments were carried out in the same apparatus, fitted with a coloured ($\lambda_{tr} > 450$ nm) lamp filter. Short wavelength irradiations were carried out in quartz tubes (20 ml) which were flushed with argon or oxygen, serum capped and irradiated by means of six external 6 W low pressure mercury lamps.

The photolysed solutions were evaporated and the residue chromatographed on silica gel eluting with light petroleum ether–diethylether (or methyl acetate) mixtures.

4.1. Isolated products

1-Phenyl-3-(2,4,6-trimethylphenyl)pyrazole (**4**). Colourless crystals, m.p. 48 °C (Light petroleum ether) (Found: C, 82.2, H, 7.0, N, 10.5%. Calcd for $C_{18}H_{18}N_2$: C, 82.40, H, 6.92, N, 10.68) δ_H ($CDCl_3$) 2.2 (s, 6H), 2.32 (s, 3H), 6.33 (d, 1H, J 2), 6.92 (s, 2H), 7.25 (m, 1H), 7.75 (m, 2H), 8.02 (d, 1H, $J = 2$). ν/cm^{-1} 1500.

1-(4-Diethylaminophenyl)-3-(2,4,6-trimethylphenyl)-pyrazole (**5**). Colourless crystals, m.p. 82 °C. (Found: C, 79.1, H, 8.0, N, 12.6. Calcd for $C_{22}H_{27}N_3$: C, 79.24, H, 8.16,

N, 12.60). δ_H 1.18 (t, 6H, $J=7$), 2.2 (s, 6H), 2.32 (s, 3H), 3.38 (q, 4H, $J=7$), 6.3 (d, 1H, $J=2$), 6.7 (d, 2H, $J=8$), 6.92 (s, 2H), 7.52 (d, 2H, $J=8$), 7.75 (d, 1H, $J=2$) ν/cm^{-1} 1500.

1-(4-Ethylaminophenyl)-3-(2,4,6-trimethylphenyl)-pyrazole (**6**). Colourless crystals, m.p. 85 °C. (Found: C, 78.8, H, 7.5, N, 13.6. Calcd for $C_{20}H_{23}N_3$: C, 79.05, H, 7.59, N, 13.76). δ_H 1.28 (t, 3H, $J=7$), 2.18 (s, 6H), 2.32 (s, 3H), 3.18 (q, 2H, $J=7$), 6.3 (d, 1H, $J=2$), 6.65 (d, 2H, $J=8$), 6.9 (s, 2H), 7.5 (d, 2H, $J=8$), 7.82 (d, 1H, $J=2$) ν/cm^{-1} 1500.

1-(4-Morpholinophenyl)-3-(2,4,6-trimethylphenyl)-pyrazole (**7**). Colourless crystals, m.p. 110–115 °C (cyclohexane–benzene) (Found: C, 76.0, H, 7.2, N, 12.0, Calcd for $C_{22}H_{25}N_3O$: C, 76.05, H, 7.25, N, 12.10). δ_H 2.18 (s, 6H), 2.3 (s, 3H), 3.18 (m, 4H), 3.82 (m, 4H), 6.4 (d, 1H, $J=2$), 6.4 (d, 1H, $J=2$), 6.92 (s, 2H), 7.08 (d, 2H, $J=3$), 7.72 (d, 2H, $J=8$), 8.3 (d, $J=2$) ν/cm^{-1} 1500.

4.2. Radical oxidation

A solution of pyrazoline **3** (50 mg) and *N*-bromosuccinimide in 4 ml acetonitrile was flushed with argon and then refluxed for 5 min. The greenish solution was evaporated and the residue chromatographed as above to yield 30 mg compound **7**.

4.3. Measurements

Oxidation potentials were voltammetrically measured by Prof. T. Soldi, University of Pavia, who is gratefully thanked. Fluorescence spectra were measured by means of a Perkin-Elmer self-corrected fluorimeter. Rate constants for the quenching of singlet oxygen were determined by laser pulse spectroscopy, by measuring the emission lifetime at 1.27 μm after oxygen sensitization by phenalenone [27].

Acknowledgements

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