On the Phosphorescence of 1*H*-Phenalen-1-one

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Dedicated to Professor *André M. Braun*, on the occasion of his 60th birthday

Combining the effects of heavy atom and low temperature, the phosphorescence spectrum from 1*H*-phenalen-1-one has been unveiled. The 0-0 band is located at 649 nm in methylcyclohexane and shifted to 646 nm in ethanol, which sets the triplet-energy level to 185 and 186 kJ · mol^{-1}, respectively. The emission is unambiguously identified as phosphorescence originating from 1*H*-phenalen-1-one through complementary transient absorption and emission studies. The quantum yield for triplet formation is confirmed to be unity.

1. Introduction. – 1*H*-Phenalen-1-one (hereafter phenalenone, also called perinaphthenone, PN) is a universal reference for sensitization of singlet oxygen, $O_2(a^1\Delta_g)$, owing to its solubility in a large variety of solvents and its high quantum yield for singlet oxygen production, Φ_Δ, which is close to 0.95 in most solvents investigated so far ranging from H_2O to cyclohexane [1–5]. Another important property of PN is its high photostability and its low rate constant for $O_2(a^1\Delta_g)$ quenching, *e.g.*, 3.2×10^4 $\text{M}^{-1}\text{s}^{-1}$ in perfluorodecalin [6]. The molecular structure and absorption spectrum are shown in *Fig. 1.*

The triplet-energy value of PN, E_T, remains a matter of debate in the literature. In 1991, *Oliveros et al.* proposed a value of 220 kJ mol^{-1} for the triplet energy, derived from phosphorescence measurements [1]. It was later shown that their emission originated from a PN photoproduct (*vide infra*). By laser-induced optoacoustic spectroscopy, *Schmidt et al.* determined a second value of 186 ± 5 kJ mol^{-1} in toluene [3]. By the same technique, though a different detector arrangement and data-handling procedures, our group obtained a similar value, 178 ± 8 kJ mol^{-1} [4]. It is important to point out that both works derived the E_T value assuming a triplet quantum yield Φ_T of unity, since laser-induced optoacoustic spectroscopy only affords the value of the product $\Phi_T E_T$. However, the value reported by *Schmidt et al.* is probably close to the correct one, since, later, *Schmidt* and *Bodesheim* were able to observe a transient emission at 650 nm, which they identified as PN phosphorescence on the basis of its quenching by oxygen [7]. In fact, the authors demonstrated in their paper that PN is able to photosensitise singlet *sigma* oxygen, $O_2(b^1\Sigma_g^+)$, which lies at 157 kJ mol^{-1}. This value should, therefore, be regarded as a lower limit for phenalenone's triplet energy. The lack of spectral information in their work still leaves open the question of where the triplet-energy level lies.

Recently, by emission spectroscopy at 77 K, *Okutsu et al.* showed that the emission reported by *Oliveros et al.* was due to a photoproduct formed by abstraction of a solvent

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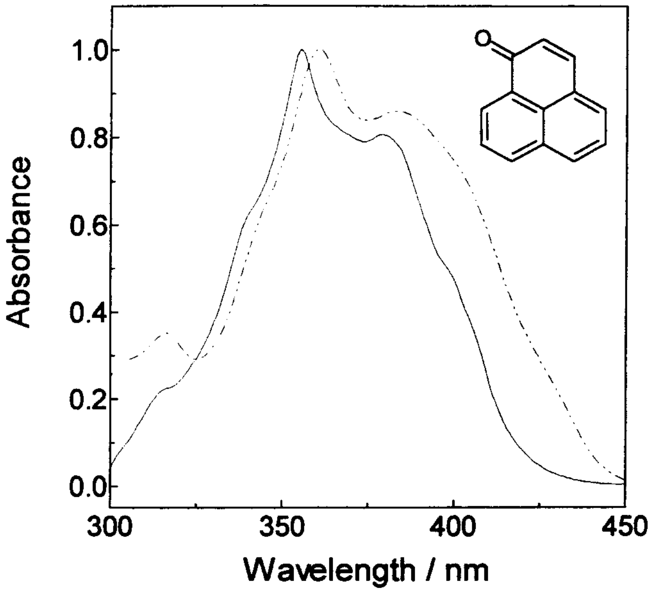

Fig. 1. *Molecular structure and absorption spectrum of phenalenone in methylcyclohexane* (continuous line) *and in EtOH* (dashed line)

hydrogen by the C=O group of PN and concluded that PN was not phosphorescent [8]. They also used another photothermal method, *i.e.*, time-resolved thermal lensing, to determine the triplet-energy level and proposed an upper-limit value of 164 kJ mol^{-1}. This is, however, in conflict with the opto-acoustic values referred to above. Thermal lensing experiments also rely on the assumption of a triplet quantum yield of unity, and, in addition, are more prone to errors, since they require a high focusing of the excitation beam, which may lead to unwanted ground-state depletion or biphotonic absorption processes.

Thus, it appears that some uncertainty still remains in the position of the triplet-energy level, which is undesirable for a compound used as a reference. Clearly, phosphorescence is the most unambiguous method for determining triplet-energy values. We, therefore, set out to determine whether conditions do exist that allow the registration of the phosphorescence spectrum of phenalenone, thereby eliminating any uncertainty in the value of its triplet-energy level. We show in this paper that, based on a combination of the external heavy-atom effect and low temperature, the phosphorescence spectrum of PN can indeed be recorded. We have used it to calculate E_T and revise the Φ_T values in the literature.

2. Results. – 2.1. *Emission Spectrum. Fig. 2* shows the emission spectrum of PN in a methylcyclohexane (MCH) and EtI 4:3 (*v*/*v*) glass at 77 K.

Two band systems can be clearly observed. The 430-to-630-nm region is essentially identical to the PN fluorescence spectrum observed by *Okutsu et al.* in 'light' solvents [8]. A new emission is observed with a maximum at 649 nm, which is identified as phosphorescence on the grounds of the following observations: *i*) it disappears, when

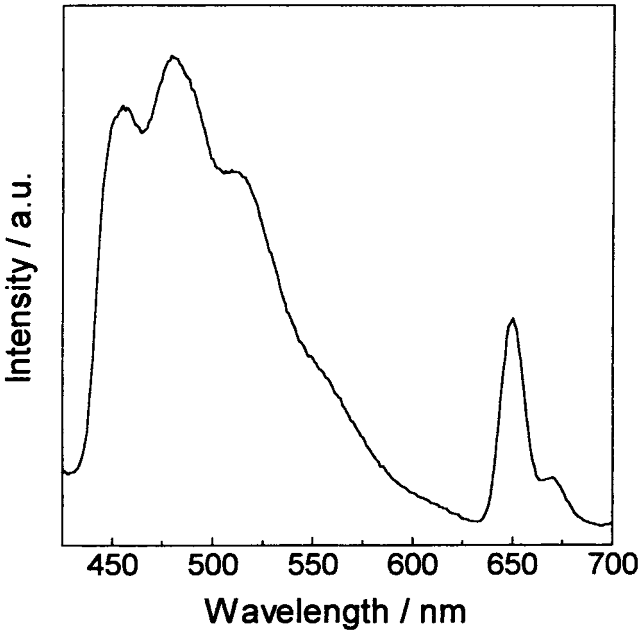

Fig. 2. *Fluorescence and phosphorescence spectrum of phenalenone in a methylcyclohexane and EtI 4:3* (*v*/*v*) *glass at 77 K.* $\lambda_{\mathrm{exc}} = 400$ nm and slit width 2 nm.

the solutions are allowed to return to room temperature, while the fluorescence bands remain; *ii*) its intensity is sensitive to the EtI contents (*vide infra*), and it disappears completely in its absence; *iii*) its lifetime is identical to that of the PN triplet as measured by transient absorption spectroscopy (*vide infra*); *iv*) its position (though not its intensity) is independent of the excitation wavelength, which rules out any artifact arising from scattered radiation.

A second concern was whether phenalenone is the emitting species. Solvent impurities were ruled out, since no signals could be detected in the absence of PN. It has already been described that PN photoproducts are fluorescent and emit in the 550–650-nm range. To rule out this emission, PN was purified by preparative TLC immediately before recording the spectra (see *Experimental*). In addition, the spectra recorded from PN samples purchased from different commercial sources were identical. As a further proof, we registered the excitation spectra of both the fluorescence (470 nm) and phosphorescence (649 nm) emissions. As shown in *Fig. 3*, the two uncorrected spectra are essentially identical, implying that the two emissions originate from the same species. A similar excitation spectrum was described by *Okutsu et al.* for the fluorescence emission [8].

2.2. *Solvent Effects.* As mentioned above, the phosphorescence emission intensity was dependent on the EtI content of the solvent mixture. *Fig. 4, A*, shows the spectra recorded for optically-matched solutions of PN in glasses of methylcyclohexane/EtI containing different amounts of the heavy-atom solvent. It can be observed in the inset that increasing the EtI proportion produces a steady decrease of the fluorescence

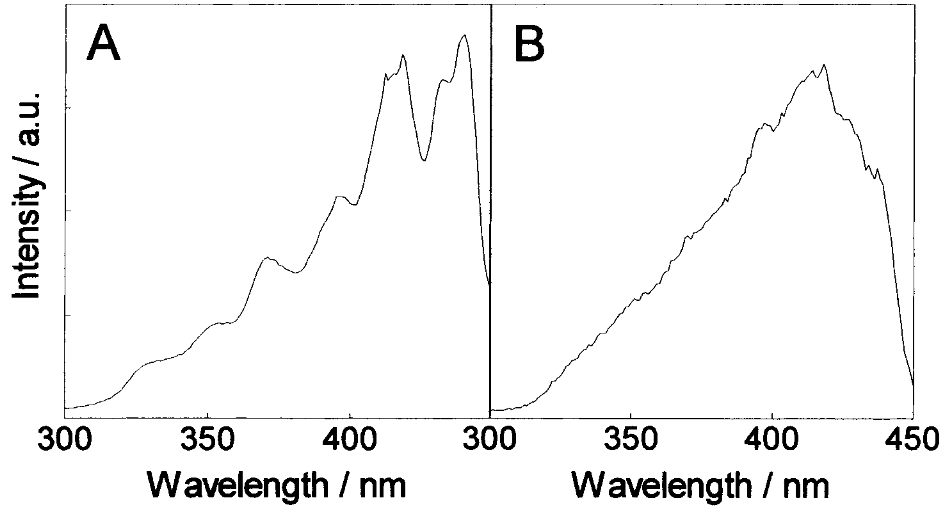

Fig. 3. *Luminescence excitation spectrum in a methylcyclohexane and EtI 4:3 (v/v) glass at 77 K. A)* λ_{obs} = 470 nm (fluorescence maximum); *B)* λ_{obs} = 649 nm (phosphorescence maximum).

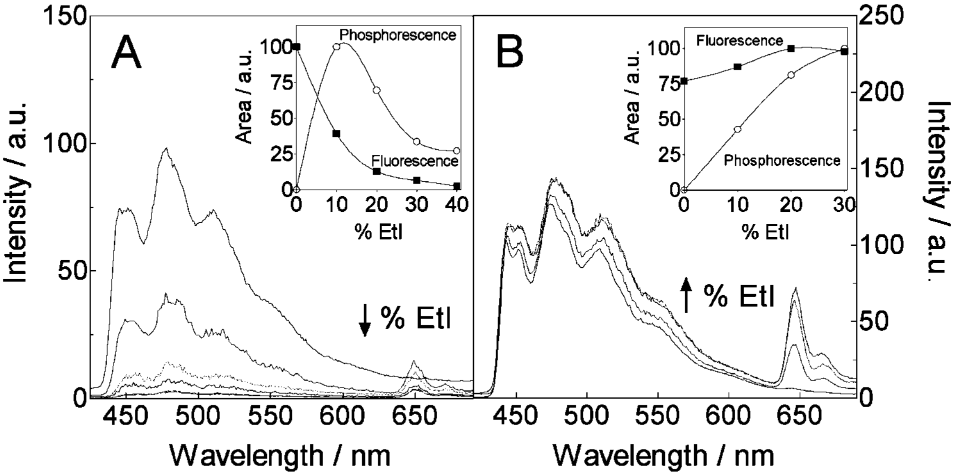

Fig. 4. *Effect of EtI contents on the fluorescence and phosphorescence intensity at 77 K. A)* In methylcyclohexane; *B)* in EtOH. In both solvents and for all mixtures, λ_{exc} = 400 nm and slitwidth 2 nm. Intensities are corrected by the refractive-index variation among the solvent mixtures. *Insets: Area under the fluorescence* (closed squares) *and phosphorescence* (open circles) *spectra normalized to the maximum value.*

intensity, while the phosphorescence band reaches a maximum and decreases at the higher EtI concentrations.

The experiment was repeated in mixtures EtOH/EtI. In this case, both emissions increased in the whole EtI concentration range, though phosphorescence increased more markedly. The phosphorescence maximum was by 2 to 4 nm blue-shifted relative to the corresponding methylcyclohexane/EtI glasses. Rough estimates of the fluorescence quantum yields at 77 K were obtained by comparison of the areas under the spectra for optically-matched solutions of phenalenone in neat methylcyclohexane or EtOH, anthracene in EtOH at 77 K (for which we assumed $\Phi_F = 0.27$), and quinine bisulfate in 1N aqueous H_2SO_4 at room temperature ($\Phi_F = 0.55$) [9]. Fluorescence quantum-yield values of 0.1 and 0.02 were thus estimated in methylcyclohexane and EtOH, respectively.

2.3. *Time-Resolution Studies.* Nanosecond laser flash photolysis studies were conducted at room temperature on solutions of PN in EtOH containing 30% EtI. In this solvent mixture, we found the highest phosphorescence emission at 77 K (see *Fig. 4, B*). Despite the fact that we were unable to observe phosphorescence under steady-state illumination conditions, we could see a transient emission with lifetime of 2.6 μs and maximum at 645 nm. This lifetime is significantly shorter than that reported in 'light' solvents, *e.g.*, 35 μs in MeOH [1], but it is nevertheless identical to the lifetime of the PN triplet in our solvent as demonstrated by the transient absorption signal at 470 nm shown in *Fig. 5*.

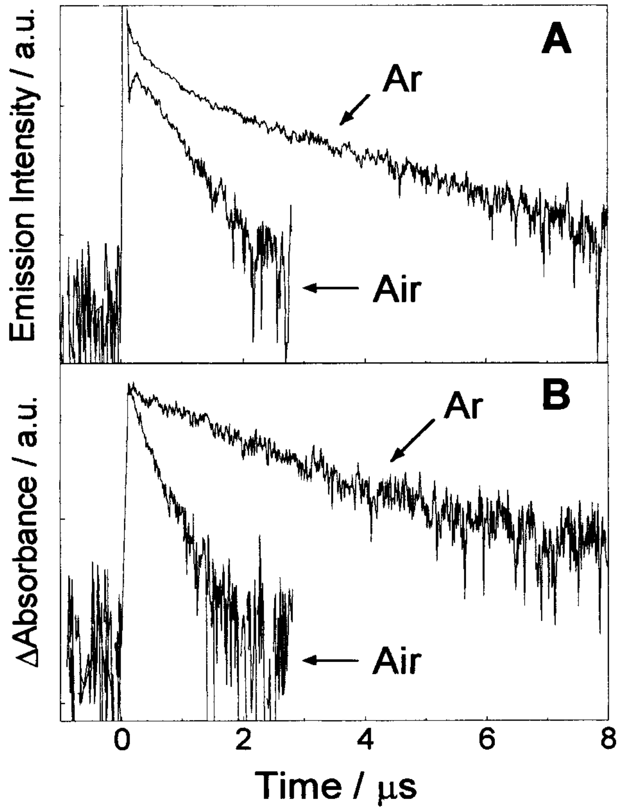

Fig. 5. *Room-temperature laser flash photolysis of PN in EtOH/EtI* (30%) *solutions* ($\lambda_{exc} = 420$ nm). *A*) Transient emission at 649 nm in Ar- and air-equilibrated solutions. *B*) Transient absorption at 470 nm in the same systems.

When the samples were equilibrated with air, the lifetimes of both absorption and emission signals were reduced to the same final value of 340 ns, which further confirms that the absorbing and emitting species is a triplet state.

3. Discussion. – Using steady-state and time-resolved emission and absorption experiments in combination with the external heavy-atom effect, the phosphorescent nature of PN has been demonstrated (*Figs. 2* and *4*). From the phosphorescence 0-0 band, we calculated a triplet-energy value of $E_T = 185$ and 186 kJ mol^{-1} in methylcyclohexane and EtOH, respectively, [10] thereby eliminating the long-lasting uncertainties in the E_T value. Our value is in excellent agreement with that of *Schmidt et al.*, i.e., $E_T = 186 \pm 5$ kJ mol^{-1} [3]. Furthermore, as their primarily determined value was the product $\Phi_T E_T = 186 \pm 5$ kJ mol^{-1}, our results also confirm their assumption of $\Phi_T = 1$, thus reducing the uncertainty in the value $\Phi_T = 1 \pm 0.1$ reported earlier by *Oliveros et al.* [1].

An attempt to rationalize the observed solvent effects is beyond the scope of this paper. Nevertheless, it is worth mentioning that phenalenone has two close-lying $\pi\pi^*$ and $n\pi^*$ singlet states, the former being more stable in polar solvents, while the situation is reversed in nonpolar ones. A similar situation holds for the triplet states, though the lowest triplet appears to be of dominant $\pi\pi^*$ character. Clearly, the solvent mixtures used span a wide range of polarities, thus changing the energy and perhaps also the electronic nature of the excited states. This alone can have a large impact on the values of the fluorescence, internal conversion, and singlet-triplet intersystem-crossing rate constants. Heavy-atom effects, in addition, are also sensitive to the electronic configuration of the states involved in the different transitions. The solvent effects collected in *Fig. 4* thus most likely reflect the balance among these effects.

Experimental. – 1*H*-Phenalen-1-one was purchased from two different sources (*Aldrich* and *Acros*) and was purified by recrystallization twice from MeOH, followed by prep. TLC with hexane/AcOEt 1:1 as eluent immediately prior to its use. All solvents used were of the highest commercially available purity and were used as received.

Absorption spectra were recorded with a *Varian Cary 4E* spectrophotometer. Steady-state 77-K fluorescence and phosphorescence spectra were recorded with a *Fluoromax-2* spectrofluorometer. Both air- and Ar-saturated PN solns. were assayed. For recording excitation spectra at 649 nm, a 550-nm cut-off filter was placed in the observation port in order to eliminate second-order grating effects. Transient absorption and emission experiments were carried out with a home-built laser-flash photolysis set-up. The 3rd harmonic of a *Continuum Surelite Nd:YAG* laser was used to pump a *Continuum OPO* laser. The ensuing laser pulses at 420 nm (10 mJ, 5 ns) were directed to a standard 10 × 10 mm fluorescence quartz cuvette containing Ar-saturated solns. of phenalenone. The samples were subjected to 10–100 pulses of laser light in order to increase the signal-to-noise ratio. For phosphorescence studies, the emission was detected at right angles by a *Hamamatsu R928* photomultiplier tube after passing through a 625-nm cut-off filter and a *PTI 101* monochromator. The detector output was fed to a *Lecroy 9410* digital oscilloscope through a 50 Ω resistor, and finally acquired by a PC for storage and analysis. For transient absorption studies, the sample absorbance changes were probed at right angles by a *CW* Xe lamp (*PTI*, 75 W), with the same detection system as described above with an appropriate pair of cut-off filters placed before (to prevent sample photodegradation) and after the cuvette (to eliminate scattered laser light).

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