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# A steady-state and time-resolved absorption and emission study of 3-thienyl-phenyl ketone, 3,3′-di-thienyl ketone and 2,3′-di-thienyl ketone

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## Abstract

To complete the photophysical study on the series of di-thienyl-ketone and thienyl-phenyl-ketone isomers, the absorption and emission properties of three compounds (3-thienyl-phenyl ketone, 2,3′-di-thienyl ketone and 3,3′-di-thienyl ketone) were investigated. Phosphorescence was observed in both, fluid solutions and frozen glasses. Intersystem crossing yields were determined by triplet sensitization measurements; effective spin–orbit coupling was found. Triplet–triplet absorption spectra, triplet lifetimes and reactivity in oxygen-quenching and self-quenching processes were investigated by nanosecond laser-flash photolysis. The lowest electronic transitions were assigned. The $S_1$ state is of $n,\pi^*$ character for all three molecules, while the lowest triplet is of $\pi,\pi^*$ configuration for the 2,3′-di-thienyl ketone and of $n,\pi^*$ configuration for the other two molecules. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Thienyl ketones; Photophysics; Laser-flash photolysis; Phosphorescence; Excited states

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## 1. Introduction

The photophysics of thienyl ketones has been investigated for a number of years by both stationary and time-resolved absorption and emission techniques [1–4].

Photochemistry and photophysics of aromatic ketones generally originate from the lowest triplet state of $n,\pi^*$ configuration. Introducing electron-donating groups may change the lowest triplet from $n,\pi^*$ to $\pi,\pi^*$, thus changing the properties and reactivity of the excited state. This change was observed in the three 2-thienyl-pyridyl ketone isomers [3] and in 2-thienyl-phenyl and 2,2′-di-thienyl ketones [1], where the carbonyl is bonded to the 2 position of a thienyl group.

In this paper, three thienyl ketones, that is, 3-thienyl-phenyl ketone (3-TPhK), 2,3′-di-thienyl ketone (2,3′-DTK) and 3,3′-di-thienyl ketone (3,3′-DTK), were investigated in order to complete the study of all thienyl-phenyl and di-thienyl-ketone isomers, represented by the general formulas of Scheme 1.

It is known from conformational studies reported in the literature [5–7], that in phenyl-thienyl and di-thienyl ketones the sulfur linked in 2 position is always on the same side of the carbonyl group, with which the thienyl ring is almost coplanar. When sulfur is in the 3 position, its preferred location is on the opposite side of the carbonyl. In the thienyl-phenyl ketones, the phenyl ring is twisted with respect to the plane of the C=O bond; thus, the extent of π-conjugation with the carbonyl is greater for the heteroaromatic ring [6]. Electronic absorption measurements and theoretical calculations support the hypothesis that π-conjugation does not extend over the whole molecule, but involves the thienyl ring which is coplanar with the carbonyl bond [8–11].

Investigations on the triplet states of these and similar molecules were carried out by Arnold et al. [12,13] They reported the energy of the 3-TPhK triplet, determined by phosphorescence measurements in various matrices at 77 K, and found that the rate of phosphorescence decay was not described by a single exponential function [13]. They assigned the lowest triplet state of 3-TPhK to an $n,\pi^*$ configuration. Substituted thienyl ketones of pharmacological interest were also investigated by stationary and pulsed techniques [14–17].

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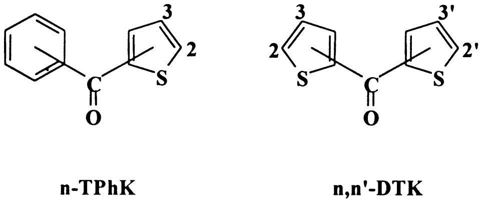

Scheme 1.

In previous investigations, we found that, like most aromatic ketones, the 2-TPhK and 2,2′-DTK, have the lowest singlet states of n,π* character, while their triplet states are π,π* [1]. In the case of the thienyl-pyridyl ketones, the triplet state could be *n*,π* or π,π*, depending on the position of the sulfur atom with respect to the carbonyl [2,3].

Independently of the triplet nature, however, all thienyl ketones exhibit room temperature phosphorescence emission, even if with very low quantum yield ($\Phi<10^{-3}$ [1,2]), and abstract hydrogen from a suitable donor; the 2-thienyl ketones are less efficient than 3-thienyl ketones in this process [4].

In order to gain a complete, overall view of the photophysics of the molecular classes represented in Scheme 1, the 3-TPhK, 2,3′-DTK and 3,3′-DTK were investigated. The absorption spectra of these molecules were recorded in solvents of different polarities. Ground-state and excited-state dipole moments were evaluated. Triplet state properties (energy, quantum yield and lifetime) were determined through phosphorescence measurements at room temperature and liquid nitrogen temperature. Spectra and decay dynamics of the transients produced by nanosecond laser-flash photolysis in mono-molecular and bi-molecular processes (self-quenching and quenching by oxygen) were investigated.

The results from this work underline the importance of the position (2 or 3) of thienyl sulfur with respect to the carbonyl on the photophysical properties of this class of ketones.

## 2. Experimental

### 2.1. Materials

The three thienyl ketones were synthesized according to methods available in the literature [2,18] and carefully purified by sublimation in vacuo. Camphorquinone (Aldrich product) was crystallized from cyclohexane and then sublimated in vacuo. Benzophenone (Carlo Erba product) was crystallized twice from water–ethanol before use.

The solvents, acetonitrile and cyclohexane were Uvasol Fluka products; 1,2-di-chloroethane and ethylacetate were Carlo Erba RS products and were used without further purification.

The solvents used for the measurements in matrix at the low temperature, EPA (ethyl-ether/*iso*-pentane/ethanol; 5/5/2 v/v), were reagent grade Fluka products.

### 2.2. Equipment and experimental conditions

The absorption spectra were recorded on a Perkin–Elmer Lambda 16 spectrophotometer. The emission measurements were carried out on a Spex Fluorolog-2 FL112 spectrofluorimeter controlled by the SPEX DM3000F spectroscopy software. For the measurements at 77 K an Oxford Instruments cryostat was used. Phosphorescence lifetimes longer than 5 μs (error limit±10%) were determined using the time-resolved unit of the Spex fluorimeter. The emission quantum yields ($\Phi_P$) were determined using benzophenone in acetonitrile and quinine bi-sulphate in 0.5 M $H_2SO_4$ as standards. The solutions were de-oxygenated by bubbling with nitrogen. Sample concentrations were adjusted in order to keep the absorbance within 0.2–0.5. The solvent contribution to the emission signal was subtracted, when necessary. The estimated uncertainty on the $\Phi_P$ values was ca. 20%, due to their small values ($\leq 10^{-4}$).

The intersystem crossing yields were determined from measurements of camphorquinone sensitized phosphorescence, at room temperature, by using the appropriate Stern–Volmer equation and taking benzophenone ($\Phi_{ISC}=1$ [19]) as a reference molecule in acetonitrile and the 2,2′-DTK ($\Phi_{ISC}\sim 1$ [1]) in cyclohexane, since benzophenone abstracts hydrogen from the hydrocarbon more efficiently than 2,2′-DTK and, therefore, its emission is strongly quenched. Data from the sensitization measurements were corrected for trivial absorption by the quencher of the exciting and emitted light. All measurements were reproduced at least twice. The uncertainty in the $\Phi_{ISC}$ values determined was within 10%.

For laser-flash photolysis measurements, the third harmonic (355 nm) from a Continuum Surelite Nd-YAG laser was used. The laser energy was <5 mJ per pulse; the time resolution was ca. 10 ns. The spectrophotometric analyzing system was made up of a 150-W Xenon source, a Baird–Tatlock monochromator blazed at 500 nm, a Hamamatsu R928 photomultiplier and a Tektronix DSA 602 digitized analyzer. The data were processed by a Tektronix PEP 301 computer. The expected accuracy in lifetime was within 10%. Suitable Q-switch delays were chosen to reduce the laser intensity in order to minimize triplet–triplet annihilation. Transient absorption spectra were recorded in point-by-point fashion. Ketone concentrations were of the order of $1.5\times10^{-3}$ mol dm$^{-3}$, corresponding to absorbances of ca. 0.6–0.8 at the exciting wavelength. For the determination of the self-quenching rate constants, the sample concentrations ranged from $10^{-3}$ to $10^{-2}$ mol dm$^{-3}$. Computerized graphical software programs were used to calculate mono- and bi-exponential decay rate constants. Even when there was significant overlap of absorption spectra of different transients (bi-exponential decay), the determinations of the rate constants at different wavelengths were in agreement within 10%.

Rate constants for transient quenching by oxygen, $k_{ox}$, were determined using oxygen-free, air-saturated and oxygen-saturated solutions.

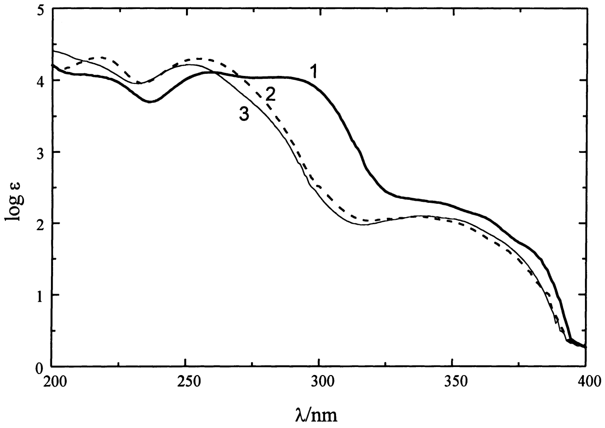

Fig. 1. Absorption spectra of 2,3′-DTK (1), 3,3′-DTK (2) and 3-PhK (3) in cyclohexane at room temperature.

## 3. Results

### 3.1. Absorption spectra

The absorption spectra of the synthesized compounds were recorded in four solvents of different polarities, chosen on the basis of their dielectric constants, $D$, and solvent-polarity parameter $E_T(30)$ of Dimroth [20]: cyclohexane (CH), $D$=2.02, $E_T(30)$=33.2, ethylacetate (EA), $D$=6.02, $E_T(30)$=38.1; 1,2-dichloroethane (DCE), $D$=10.36, $E_T(30)$=41.9; and acetonitrile (ACN), $D$=37.5, $E_T(30)$=46.0.

Like most aryl ketones, the three molecules investigated exhibit two distinct absorption regions (Fig. 1): an intense absorption ($\log\varepsilon\approx4$) at short wavelength ($\lambda<300$ nm) and a weaker band ($\log\varepsilon\approx2$) at longer wavelength ($\approx$350 nm). The lower energy band becomes fairly structured at low temperatures (see below): the vibrational spacing, $\Delta\nu\sim1200\,\text{cm}^{-1}$, corresponds to the carbonyl stretching in the excited state [21]. The absorption maxima and molar absorption coefficients of the three compounds in four solvents at room temperature are reported in Table 1.

With increased solvent polarity, the higher energy band shifts to the red, while the lower-energy transition shifts to the blue. Based on location and shape of spectra, molar absorption coefficients and solvent effect, the higher energy absorption region is assigned to π,π* transitions, while that at lower energies is assigned to $n$,π* transitions. For the 2,3′-DTK only, an additional band is observed in the spectral region of the π,π* absorption ($\lambda_{max}$=290 nm). This band was present in all 2-thienyl ketones and was assigned to charge transfer from the 2-sulfur to the carbonyl [1,2,12]. The assignments were also supported by plotting the spectral data as a function of the Dimroth solvent parameter ($E_T$ 30): given the broadness of the bands, the experimental wavelength maxima were used for these plots. Straight lines were obtained with positive slopes for the $n$,π* transitions and negative slopes for the π,π* transitions.

Table 1
Absorption maxima, $\lambda_{max}$ (nm), and molar absorption coefficients ($\log\varepsilon$) of the TKs in various solvents at room temperature

| Compound | CH | EA | DCE | ACN |
|---|---|---|---|---|
| 3-TPhK | 251 (4.20)<br>339 (2.10) | 257 (4.14)<br>335 (2.15) | 255 (4.19)<br>333 (2.24) | 254 (4.15)<br>331 (2.19) |
| 3,3′-DTK | 255 (4.29)<br>337 (2.09) | 256 (4.29)<br>335 (2.18) | 258 (4.26)<br>333 (2.25) | 257 (4.23)<br>332 (2.29) |
| 2,3′-DTK | 258 (4.10)<br>287 (4.04)<br>345 (2.29) | 261 (4.05)<br>289 (4.03)<br>342 (2.41) | 262 (4.07)<br>292 (4.04)<br>341 (2.35) | 260 (4.05)<br>291 (4.03)<br>340 (2.35) |

The solvent-shift method was used to evaluate the excited state dipole moments, while the ground-state dipole moments were calculated by optimizing the molecular geometries, using a semi-empirical modeling program (PM3) and then carrying out a search for the lowest energy conformation [22]. The plot of the Kawski–Gryczynski relationship was used, Eq. (1) [23–25], where

$$-\Delta\nu_{1\text{–}2} = 2\mu_g\frac{(\mu_{exc}-\mu_g)}{hca^3}\times\Delta f_{1\text{–}2}(D,n) \tag{1}$$

where $-\Delta\nu_{1\text{–}2}$ is the shift of the absorption band between solvents of different dielectric constants, $D$, and refractive indexes, $n$, $\mu_g$ and $\mu_{exc}$ the dipole moments of the molecule in the ground and excited states, respectively, $h$ the Planck's constant, $c$ the velocity of light, $a$ the Onsager cavity radius and $f_{1\text{–}2}$ ($D$,$n$) a function of the dielectric constant and refractive index of the solvent given by the equation:

$$f(D,n) = \frac{(2n^2+1)}{(n^2+2)}\left[\frac{(D-1)}{(D+2)} - \frac{(n^2-1)}{(n^2+2)}\right] \tag{2}$$

The Onsager cavity radius (3.3–3.5 Å) was calculated for each molecule using the Hyperchem software. The dipole moments in the excited states were estimated from the slope of the linear plots of $-\Delta\nu_{1\text{–}2}$ as a function of $\Delta f_{1\text{–}2}(D,n)$, Fig. 2, and the calculated $\mu_g$ values. The ground-state and

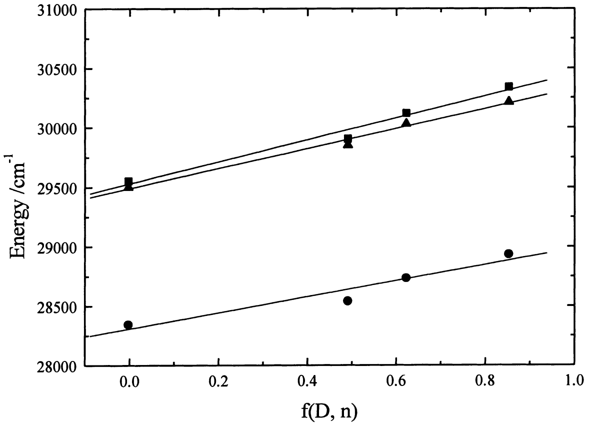

Fig. 2. Correlation diagrams of the singlet $n$,π* energies with the solvent parameter of Eq. (2): (●), 2,3′-DTK; (▲), 3-TPhK; and (■), 3,3′-DTK.

Table 2
Dipole moments (debyes) of the TKs in the ground state and $n,\pi^*$ and $\pi,\pi^*$ singlet excited states

| | 3-TPhK | 3,3′-DTK | 2,3′-DTK |
|---|---|---|---|
| $\mu_g$ | 2.5 | 2.3 | 2.8 |
| $\mu_{exc}^{n,\pi^*}$ | 1.2 | 0.8 | 1.9 |
| $\mu_{exc}^{\pi,\pi^*}$ | 3.6 | 3.5 | 3.6<br>4.0 |

Table 3
Photophysical parameters of the TKs determined from emission measurements at room temperature in acetonitrile and cyclohexane

| | Acetonitrile | | | | Cyclohexane | | | |
|---|---|---|---|---|---|---|---|---|
| | $\Phi_{ISC}$ | $\Phi_P$ | $\tau_P$ (μs) | $k_P$ ($s^{-1}$) | $\Phi_{ISC}$ | $\Phi_P$ | $\tau_P$ (μs) | $k_P$ ($s^{-1}$) |
| 3-TPhK | 0.8 | $1.4\times10^{-4}$ | 10 | 17 | 0.4 | $1.4\times10^{-4}$ | 8 | 44 |
| 3,3′-DTK | 0.6 | $8.0\times10^{-5}$ | 12 | 11 | 0.3 | $4.6\times10^{-5}$ | 7 | 22 |
| 2,3′-DTK | 1.0 | $7.7\times10^{-5}$ | 13 | 6 | 0.8 | $1.3\times10^{-4}$ | 10 | 16 |

excited-state dipole moments are reported in Table 2. The $\mu_g$ values are close to those of benzophenone, pyridyl ketones and thienyl-pyridyl ketones [2,26]. The decrease of dipole moments upon $n,\pi^*$ singlet excitation is less for the 2,3′-DTK (0.9 debyes) than for the other two molecules (ca. 1.4 debyes). This behavior indicates reduced perturbation of the $n,\pi^*$ singlet state by the upper $\pi,\pi^*$ one when the sulfur is in 3 position. An analogous difference was also found between 2- and 3-thienyl-pyridyl ketones [2]. The $\mu_{exc}^{\pi,\pi^*}$ values are more uncertain due to worse correlation of the plot of Eq. (1); however, as expected, they are greater than both ground state and $n,\pi^*$ excited state dipole moments. In particular, the highest $\mu_{exc}^{\pi,\pi^*}$ for the lowest $\pi,\pi^*$ transition of the 2,3′-DTK is in agreement with the CT character assigned to this state.

### 3.2. Emission spectra

Since room temperature emission spectra of 3-TPhK and DTKs, with maxima in the 450–500 nm range, were detected only in oxygen-free solutions, they were assigned to phosphorescence, while fluorescence was undetectable. Emission spectra, quantum yields ($\Phi_P$) and lifetimes ($\tau_P$) were determined in a polar solvent (ACN) and in a non-polar (CH) solvent. Emission spectra in ACN are shown in Fig. 3; excitation spectra were found to match the absorption spectrum well. No significant solvent effect is evident: all spectra are broad and structureless, the quantum yields are small ($10^{-4}$–$10^{-5}$) and the lifetimes are of the order of 10 μs. Results for all molecules are reported in Table 3.

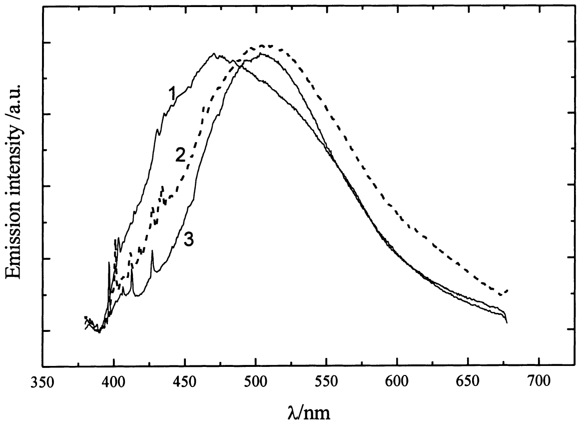

Fig. 3. Room-temperature phosphorescence emissions in oxygen free ACN solution: 1, 3,3′-DTK; 2, 3-TPhK; 3, 2,3′-DTK.

The intersystem crossing yields were determined in both solvents by measuring the sensitized phosphorescence of camphorquinone, which has a suitable triplet energy since it exhibits room temperature phosphorescence shifted to the red ($E_T$=210 kJ mol$^{-1}$ [27]) compared to those of TKs ($E_T$>260 kJ mol$^{-1}$, see later). The $\Phi_{ISC}$ values are rather high, particularly in ACN, but not unitary, while those of 3-TPhK and 3,3′-DTK in CH are reduced by half. The decreased population of the triplet in a hydrocarbon solvent may be due to hydrogen abstraction from the solvent by the ketone $n,\pi^*$ singlet [28]. The occurrence of this process is also in agreement with the marked decrease in dipole moment for these two molecules upon excitation, indicating decreased charge density to the carbonyl. The rate coefficients for phosphorescence emission, $k_P$, were obtained from the intersystem crossing and phosphorescence quantum yields and the experimental lifetimes ($\tau$), using the relationship:

$$k_P = \frac{\Phi_P}{(\Phi_{ISC} \times \tau)} \qquad (3)$$

The parameters obtained from phosphorescence measurements in the two solvents at room temperature are reported in Table 3.

In a rigid matrix (EPA) at low temperature (77 K), all three thienyl ketones exhibited fairly intense phosphorescence emissions. The emissions of the three ketones differed in lifetime and vibronic structure.

#### 3.2.1. 3-TPhK

The emission and emission excitation spectra of 3-TPhK in EPA at 77 K are shown in Fig. 4. The emission is typically of $n,\pi^*$ character with a well-resolved vibronic progression ($\Delta\nu$~1700 cm$^{-1}$), such as that reported by Arnold [13]. The decay was clearly mono-exponential and the lifetime was relatively short ($\tau$=5.5 ms). In the excitation spectrum, the vibronic carbonyl sequence of the excited singlet state is much better resolved than in the room-temperature absorption and allows the $S_0 \rightarrow S_1$ band ($E_{S_0 \rightarrow S_1}$=328 kJ mol$^{-1}$) to be identified easily.

#### 3.2.2. 3,3′-DTK

As can be seen from Fig. 5, the phosphorescence emission of the 3,3′-DTK is quite different and appears to be

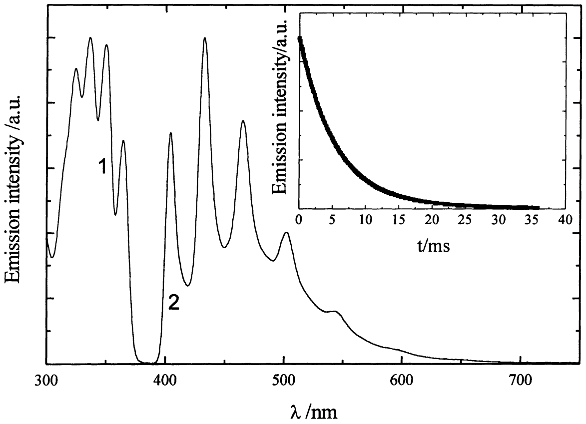

Fig. 4. Phosphorescence excitation (1) and phosphorescence emission (2) spectra of 3-TPhK in EPA at 77 K. Insert: first-order decay kinetics.

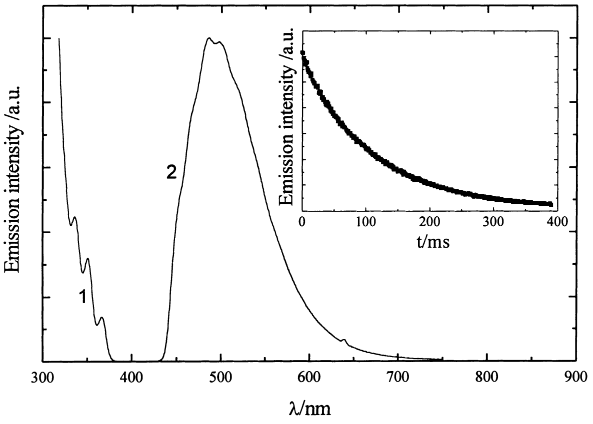

Fig. 6. Phosphorescence excitation (1) and phosphorescence emission (2) spectra of 3,2′-DTK in EPA at 77 K. Insert: first-order decay kinetics.

due to the overlapping of two distinct transitions. The higher energy transition is revealed by a neat peak and a shoulder ($\Delta\nu\sim1700\,\mathrm{cm}^{-1}$, carbonyl stretching) on the blue side of the lower energy band which is broad and more intense. The emission decay is bi-exponential, with a short component ($\tau=2.7$ ms) and a longer component ($\tau=16$ ms), which contribute to total emission intensity by about the same amount (the pre-exponential factors of the fit are almost equal). The excitation spectrum shows the typical shape of an $n,\pi^*$ transition. In addition, by using high-sensitivity instrumental conditions, a method previously proposed by Kearns et al. [29–31], the spin-forbidden $S_0\rightarrow T_1$ absorption ($E_{S_0\rightarrow T_1}=299\,\mathrm{kJ\,mol}^{-1}$) could also be detected in the emission excitation spectrum. This transition fairly overlapped the 0–0 band in the phosphorescence spectrum.

### *3.2.3. 2,3′-DTK*

The carbonyl progression was no longer present in the 2,3′-DTK emission spectrum and the vibronic structure was hardly detectable (Fig. 6). The decay was mono-exponential, indicating a unique phosphorescent state with a fairly long lifetime ($\tau=110$ ms). The emission is assigned to the $\pi,\pi^*$ $T_1\rightarrow S_0$ transition, based on the long lifetime and poor vibronic structure, while the vibronic structure in the excitation emission spectrum indicates an $n,\pi^*$ state ($E_{S_0\rightarrow S_1}=325\,\mathrm{kJ\,mol}^{-1}$).

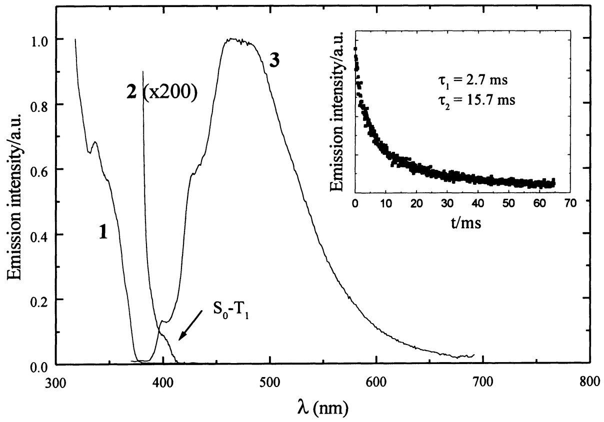

Fig. 5. Phosphorescence excitation (1, 2) and phosphorescence emission (3) spectra of 3,3′-DTK in EPA at 77 K. Insert: bi-exponential decay kinetics.

The spectral and kinetic data obtained in EPA at 77 K for the three thienyl ketones are reported in Table 4.

### *3.3. Laser flash photolysis measurements*

Upon nanosecond laser excitation ($\lambda=355$ nm) of TKs in ACN solution at room temperature, the triplet states were produced and characterized by their absorption spectra, lifetimes, oxygen-quenching and self-quenching. The transient spectra and dynamic behavior of 3,3′-DTK and 3-TPhK were more similar to each other than to those of 2,3′-DTK.

### *3.3.1. 3,3′-DTK and 3-TPhK*

The time-resolved spectra of these two molecules show the simultaneous presence of two transients, $T_1$ and $T_2$, both with triplet characteristics. The presence of two transients was revealed by the bi-exponential decay profiles and the time dependence of the spectral shape. Since both triplets absorb over the whole spectral region investigated, the kinetic constants were obtained by bi-exponential fit of the decay curves.

One of the triplets, $T_1$, is shorter-lived ($\tau_1=0.34\,\mu$s for the 3-TPhK and 0.15 μs for the 3,3′-DTK ) than the other ($\tau_2=9.3\,\mu$s and 2.8 μs for 3-TPhK and 3,3′-DTK, respectively). Due to this lifetime difference, the spectra recorded a few hundred nanoseconds after the laser pulse substantially represent the neat absorptions of the longer-lived triplets, $T_2$, as shown in Fig. 7 for the 3,3′-DTK. For both molecules, the spectrum of $T_1$ is characterized by maxima at ~500 and ~700 nm, that are no longer present after 0.3 μs, while the residual absorption due to $T_2$ consists of two bands around 370 and 600 nm. Both $T_1$ ($k_{\mathrm{ox}}\sim5\times10^9\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$)

Table 4
Spectral and kinetic parameters of TKs determined from emission measurements in EPA at 77 K

| | $\lambda_{max}(T)$ (nm) | $\Delta\nu$ (cm$^{-1}$) | $\lambda_{max}(S_1)$ (nm) | $\Delta\nu$ (cm$^{-1}$) | $\tau_P$ (ms) ($k_P$ (s$^{-1}$)) | $E_T$ (kJ mol$^{-1}$) | $E_S$ (kJ mol$^{-1}$) | $\Delta\nu$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 3-TPhK | 404 | | 364 | | 5.5 | 296 | 328 | 2720 |
| | 432 | 1600 | 350 | 1099 | (180) | | | |
| | 465 | 1640 | 336 | 1190 | | | | |
| | 502 | 1590 | 324 | 1100 | | | | |
| | 543 | 1500 | 314s | 983 | | | | |
| | 592 | 1520 | | | | | | |
| 3,3′-DTK | 399 | | 366 | | 2.7 | 299 | 327 | 2340 |
| | 428 | 1700 | 349 | 1330 | (370) | | | |
| | 465 | 1860 | 336 | 1110 | 16 | | | |
| | 485 | 890 | 322 | 1290 | (64) | | | |
| 2,3′-DTK | 455s | | 366 | | | 262 | 325 | 5350 |
| | 468s | 610 | 351 | 1170 | 108 | | | |
| | 486 | 790 | 336 | 1270 | (9.3) | | | |
| | 498 | 500 | | | | | | |
| | 518 | 780 | | | | | | |

and $T_2$ ($k_{ox}$~$1\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$) were sensitive to oxygen. The self-quenching constants, $k_{sq}$, determined for both triplets of each compound at the appropriate wavelength, are about one order of magnitude greater for $T_1$ ($k_{sq}$=$4-10\times10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) than for $T_2$ ($k_{sq}$~$2\times10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$). Spectral features, dynamic behavior and comparison with analogous molecules [3] indicate an $n,\pi^*$ character for $T_1$ and a $\pi,\pi^*$ character for $T_2$.

### 3.3.2. 2,3′-DTK

For this molecule, the principal transient, $T_1$ (Fig. 8), is characterized by two distinct absorption regions ($\lambda_{max}$= 380 and 580 nm) and a rather long lifetime ($\tau_1$=6.2 μs). This transient was efficiently quenched by oxygen ($k_{O_2}$= $1.6\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$). The self-quenching constant, $k_{sq}$, was about the same order of magnitude as that of $T_2$ in the other molecules ($k_{sq}$~$3.7\times10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$). Based on this behavior, the transient obtained from 2,3′-DTK was assigned to a triplet of $\pi,\pi^*$ character.

Spectral and kinetic parameters of the triplets of the three molecules are reported in Table 5.

## 4. Discussion

In previous works we established that the heterocyclic sulfur atom, due to its electron-donating power, determines: (i) the orbital character of the lowest triplet, which is $\pi,\pi^*$ for the 2 sulfur position and $n,\pi^*$ for the 3 sulfur position; (ii) the triplet energy (~260 kJ mol$^{-1}$, 2 position and ~290 kJ mol$^{-1}$, 3 position); and (iii) the dynamic behavior in the mono- and bi-molecular processes of the triplet state (lifetime, quenching by oxygen, self-quenching and hydrogen abstraction) [1–4].

The three molecules investigated here can be considered to be a 3-thienoyl group bonded with a phenyl (3-TPhK), a 2-thienyl (2,3′-DTK) and a 3-thienyl (3,3′-DTK). The different photophysics can be understood considering the effect of

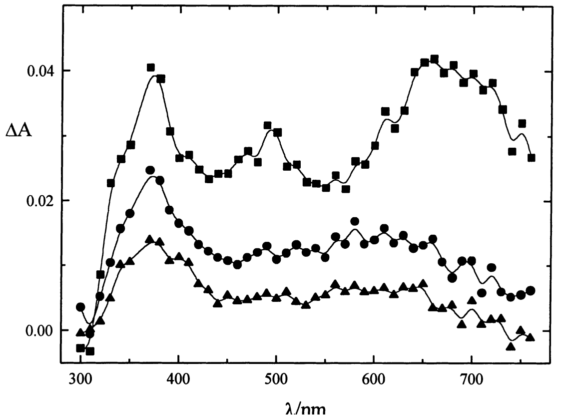

Fig. 7. Time resolved spectra of 3,3′-DTK obtained upon laser flash photolysis in ACN solution: (■), 0.03 μs; (●), 0.27 μs; and (▲), 1.60 μs delay.

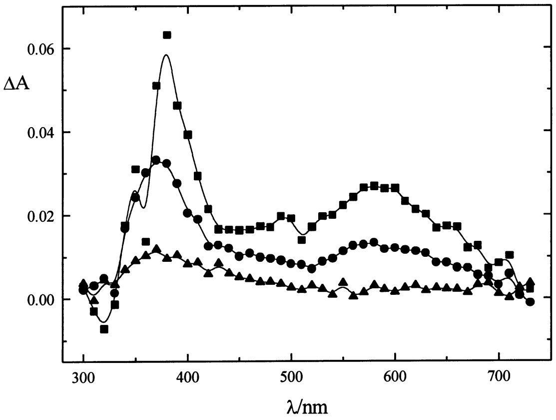

Fig. 8. Time resolved spectra of 2,3′-DTK obtained upon laser flash photolysis in ACN solution: (■), 0.08 μs; (●), 2.4 μs; and (▲), 16.0 μs delay.

Table 5
Spectral and dynamic characteristics of TKs obtained by laser flash photolysis measurements

| Compound | $\lambda_{\max}$ (nm) | | $\tau$ ($\mu$s) | | $k_{ox}\times10^9$(dm$^3$ mol$^{-1}$ s$^{-1}$) | | $k_{sq}\times10^8$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_1$ | $T_2$ | $T_1$ | $T_2$ | $T_1$ | $T_2$ |
| 3-TPhK | 350<br>490<br>680 | 370<br>620 | 0.34 | 9.3 | 5.0 | 1.2 | 3.8 | 0.22 |
| 2,3′-DTK | 370<br>490<br>660 | 370<br>580 | 0.15 | 2.8 | 3.4 | 2.2 | 9.9 | 0.23 |
| 3,3′-DTK | 380<br>580 | | 6.2 | | 1.6 | | 0.37 | |

the second ring, the electron-donor characteristic of which decreases from the 2,3′-DTK to 3,3′-DTK, to 3-TPhK. The $\sigma_+$ constants for the ring sulfur atom are $-0.79$ and $-0.52$ for the 2 and 3 positions, respectively [32]. Therefore, the thienyl group is an efficient electron-donor toward the carbonyl, especially when the sulfur is in 2 position. In contrast, the phenyl ring has a little effect and, moreover, theory strongly suggests that it is rotated with respect to the carbonyl plane, with scarce participation in the conjugate system. Consequently $\pi,\pi^*$ states are stabilized in the order:

$$2,3'\text{-DTK} > 3,3'\text{-DTK} > 3\text{-TPhK}$$

Accordingly, the results of this work indicate that the benzophenone-like behavior ($n,\pi^*$ character of the lowest singlet and triplet states, typical 'five-fingered' phosphorescence emission with lifetimes in the millisecond range in rigid matrix) decreases from the 3-TPhK to 3,3′-DTK to 2,3′-DTK.

The energy of the $n,\pi^*$ lowest singlet states (326–328 kJ mol$^{-1}$) is not appreciably affected by the structure. In contrast, while the triplet state energy is only slightly different between the 3,3′-DTK and 3-TPhK, it is much lower for the 2,3′-DTK. The small, but significant increase in the $n,\pi^*$ triplet energy ($\sim$3 kJ mol$^{-1}$) of the 3,3′-DTK compared to the 3-TPhK is in line with the electron-donor effect of the thienyl compared with the phenyl group. The marked decrease of the triplet energy in the 2,3′-DTK ($\sim$35 kJ mol$^{-1}$) is due to a significant stabilization by the 2-thienyl group of the $\pi,\pi^*$ triplet state, which is the lowest triplet. It is worth noting that the triplet energies of the 2,2′-DTK and 2-TPhK are of the same order of magnitude as the 2,3′-PTK. This means that the sulfur atom in 2 position determines the switching of the lowest triplets, as was previously found for the 2-thienyl-pyridyl ketones (2,$n'$-TPK) [3].

The behavior of the 3,3′-DTK, however, is somewhat ambiguous. The shorter decay component and $S_1$–$T_1$ separation are in favor of an $n,\pi^*$ lowest triplet, while the longer decay component and most intense lower-energy band denote $\pi,\pi^*$ characteristics. An intermediate behavior of this molecule could be expected, due to the electron-donating efficiency of the 3-thienyl group which is intermediate between those of phenyl and 2-thienyl. This implies a closer proximity of the $n,\pi^*$ and $\pi,\pi^*$ triplet states in the 3,3′-DTK than in the 3-TPhK, but not an inversion of the excited state of different configurations as occurs for the 2,3′-DTK. However, the double phosphorescence emission cannot be easily explained. Since no exciting wavelength effect on both lifetimes and relative contributions of the two components was detected, we exclude the possibility that the emissions are due to different ground state species. The most plausible hypothesis is that excited states of different orbital character ($n,\pi^*$ and $\pi,\pi^*$) are simultaneously populated by the excited singlet, without an appreciable vibronic coupling between them. This hypothesis could also explain the absorptions by two triplet states upon laser excitation. In fact, there is no spectral or kinetic evidence that $T_1$ or $T_2$ is the precursor of the other: they decay independently and interact with oxygen and the ground state itself independently, as demonstrated by the different values of the rate constants determined. A similar behavior had also been observed for the 3-thienyl-4-pyridyl ketone [3].

The occurrence of room temperature phosphorescence with a quantum yield lower than that observed for other aryl ketones (benzophenone, pyridyl ketones) is also in agreement with the idea of two quasi-independent triplets for the 3-thienyl ketones. The $n,\pi^*$ triplet is believed to be responsible for the room temperature emissions for all the molecules. In the case of the 2,3′-DTK, which has a lower-lying $\pi,\pi^*$ triplet state, the unusual room temperature phosphorescence is attributed to thermal equilibration of the $\pi,\pi^*$ triplet with the nearby $n,\pi^*$ one. This hypothesis could also explain the unexpected reactivity of 2-thienyl ketones in the hydrogen-abstraction process [4].

The differences in the self-quenching rates of the two triplets ($n,\pi^*$: $k_{sq}\sim4\times10^8-1\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $\pi,\pi^*$: $k_{sq}\sim2-4\times10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$), which were also found for the 3,4′-TPK [3] were explained by the hypothesis of a charge transfer process [33,34] where the thienyl ring in the ground-state molecule is the electron donor and the excited carbonyl the electron acceptor. More efficient self-quenching is exhibited by $n,\pi^*$ triplets due to smaller charge density on the excited carbonyl and greater charge density on the thienyl ring, since sulfur is unconjugated with the carbonyl [3].

Another point worth noting is the difference between the $k_P$ values obtained from low temperature measurements ($=1/\tau$ at 77 K) and those determined from the lifetime and quantum yields at room temperature (Eq. (3)). In the case of 2,3′-DTK these values are of the same order of magnitude, typical of a $\pi,\pi^*$ triplet ($k^0 < 10\,s^{-1}$), while for the 3-TKs, the $k_P$ values from different experimental data differ by more than one order of magnitude. We believe that the values obtained at low temperature are the true rate parameters of the $n,\pi^*$ triplets, while the room-temperature values are affected by the experimentally determined $\Phi_{ISC}$, which accounts for both the $n,\pi^*$ and $\pi,\pi^*$ triplet populations, and the experimental $\Phi_{P,}$ which only refers to the $n,\pi^*$ triplet emission.

## 5. Conclusions

The results of this work are in line with those obtained for other thienyl ketones, that is, the photophysics of these classes of molecules is mainly dictated by the position (2 or 3) of the thienyl sulfur with respect to the carbonyl.

Considering the electron donor properties of the thienyl group, which stabilizes the $\pi,\pi^*$ states, while destabilizing the $n,\pi^*$ ones, and much more if in 2 position to the carbonyl, if the triplets were in the same order as the singlets, the energy difference between such states is expected to decrease in the order:

$$\text{3-TPhK} > 3,3'\text{-DTK} > 2,3'\text{-DTK}$$

However, if these two states are close in energy, an excited state switching may occur as happens for the 2,3′-DTK, for which the lowest triplet is of $\pi,\pi^*$ character. All photophysical properties of the thienyl ketones studied are in agreement with this view.

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